ENVIRONMENTAL MONITORING AND ASSESSMENT PROGRAM: INTEGRATED QUALITY ASSURANCE PROJECT PLAN FOR SURFACE WATERS RESEARCH ACTIVITIES

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1.0 PROJECT PLANNING AND MANAGEMENT

1.1 Introduction

In response to a growing need to identify the extent, magnitude, and status (with respect to anthropogenically induced degradation) of ecological resources within the united states, the U.S. Environmental Protection Agency (EPA) Office of Research and Development (ORD), in cooperation with other federal and state organizations, implemented the Environmental Monitoring and Assessment Program (EMAP) in 1989. In 1995, EMAP was modified based on external peer reviews, ORD resource constraints, and to interface with the national interagency monitoring framework being developed by the Council on Environment and Natural Resources (CENR). The overall goal of EMAP is to develop the appropriate tools and to participate in monitoring and assessing the condition of the nation's ecological resources and to contribute to decisions on environmental protection and management (U.S. EPA, 1997). To accomplish this goal, EMAP works to attain four objectives:

- Estimate the current status, trends, and changes in selected indicators of the condition of the Nation's ecological resources on a regional basis with known statistical confidence.
- Estimate the geographic coverage extent of the Nation's ecological resources with known statistical confidence.
- Seek associations between selected indicators of natural and anthropogenic stresses and indicators of condition of ecological resources.
- Provide annual statistical summaries and periodic assessments of the Nation's ecological resources.

Monitoring and assessment tools being researched and developed for EMAP will contribute to improving ecological risk assessments. These risk assessments will provide estimates (with quantifiable uncertainty) of the effects of anthropogenic activities on the ecological resources monitored. For each type of resource, attributes of ecological condition perceived as valued or desirable by society are defined as "societal values." Because societal values generally are not amenable to direct measurement, surrogate measurements are used. These surrogate measurements, are operationally defined as "indicators" (Hunsaker and Carpenter, 1990). Indicators are any ecological measurement, metric, or index that quantifies physical, chemical, or biological condition, habitat, or stress. In EMAP, indicators are developed

from single environmental measurements or from aggregations of measurements into some type of index.

1.2 Surface Waters Activities within EMAP

Inland surface water research activities within EMAP are focused on lakes (exclusive of the great lakes), reservoirs, rivers, streams, and freshwater wetlands. The intent of EMAP is to characterize the ecological condition of these resources and evaluate the cumulative effectiveness of regulatory policies, at a regional and national scale, over many decades (Whittier and Paulsen, 1992). Most historical aquatic monitoring programs have concentrated on specific sites, pollutants, or issues. Consequently, it is not currently possible to statistically assess either the present status of surface water resources or progress towards goals of mitigating or preventing adverse ecological effects (Whittier and Paulsen, 1992). The EMAP surface waters research program has been designed to address these needs. Research efforts are conducted at two ORD laboratories, the National Health and Environmental Effects Research Laboratory (NHEERL), and the National Exposure Research Laboratory (NERL). Within NHEERL, research is conducted at the Western Ecology Division (WED), in Corvallis, OR. Within NERL, research is conducted at the Ecological Exposure research Division (EERD) in Cincinnati, Ohio.

The major long-term research objectives of EMAP listed in Section 1.1 are applied to the specific ecological resource of inland surface waters in EMAP - SW (Paulsen et al. 1991). The condition of aquatic ecosystems is assessed in EMAP - SW relative to three societal values: biological integrity, trophic state, and fishability. Biological integrity represents the ability of a system to support biotic communities having ecological structural, functional, and organizational characteristics comparable to a natural, unmanaged system within the region (Karr and Dudley 1981; Karr, 1991). Trophic state is related primarily to the degree of cultural eutrophication experienced by aquatic ecosystems, but also includes other aspects of physical or chemical impacts on water quality (e.g., contamination by toxic wastes, acidification, sedimentation, salinization, and thermal pollution). Fishability is related to the ability to harvest fish by angling and the associated edibility of the harvested fish by either human or other animal consumers (Plafkin et al., 1989).

In general, surface water research efforts will be conducted in a particular geographic region using a 4-year sampling cycle (approximately 200 site visits per year for a regional-scale

demonstration project). This provides the capability to develop and evaluate various indicators (including important components of variability) and provides an adequate sample size to conduct a regional assessment of aquatic resources. In each year, sampling locations will be selected from the EMAP sampling framework using statistical probability methods to ensure that robust population inferences can be made and that the sites are representative of the spatial distribution and size class of the nation's inland surface water resources (Whittier and Paulsen, 1992).

The indicators selected for EMAP need to be applicable across the broad geographic scale of the program. Because EMAP data will contribute to the development of regional (and eventually national) assessments, the ecological condition of inland surface waters is evaluated on populations, not on individual systems. Indicators also need to be amenable to sampling within a specific index period, as all data will be gathered during a single sampling visit conducted during a limited portion of the year. For many of the indicators selected for use in EMAP, historical information on the variability of specific measurements is not readily available. Thus part of the overall sampling design for a regional research project includes obtaining data to identify sources and quantify the magnitude of variance components associated with specific measurements and indicators. Within EMAP, indicators may be defined as "core" (i.e., variance components well-defined, indicator measurements have a direct relationship to societal values) or "candidate" (i.e., variance components and/or relationship to societal values as yet not clearly defined). Core status indicators generally have higher priority than candidate indicators.

The goal of the an EMAP regional surface water research project is to assure that all indicators be fully developed, logistics and operations optimized, and information management systems fully tested and on-line. These are accomplished through a series of pilot, demonstration, and special interest surveys within a geographic region. Pilot surveys are conducted on a subset of target sampling locations and may be conducted primarily to test logistics and methods, and/or to investigate sources of variability. Demonstration surveys are generally conducted on a regional scale, including sampling of all target sites within a specific region. The demonstration surveys provide additional testing of logistics, operations, and methods. Most involve the cooperative effort of one or more federal or state agencies within the targeted region. Special interest studies may be conducted as pre-pilot efforts (e.g., plot design studies), in conjunction with a pilot or demonstration survey, or as a separate program. Special interest studies may include intense investigation of the feasibility of a particular indicator, investigation of components of variability, or other issue which necessitates sampling on an intensive scale and/or sampling of nontarget sites.

1.2.1 Relevant Research Documentation

EMAP surface water research activities are currently guided by two research plans. The first is the EMAP-Surface Waters Monitoring and Research Strategy (Paulsen et al., 1991), The basic objectives and approaches outlined in this document remain relevant to current indicator research projects. The second research plan is that developed for EMAP (U.S. EPA, 1997), which provides how past, current, and future EMAP research efforts meet the needs of the modified program, as well as how they relate to the ORD strategic plan and the Agency's mission.

1.2.2 Scope of QA Project Plan

This QA plan primarily addresses two data acquisition efforts within EMAP. The first is a regional survey of wadeable streams in the eastern U.S. being conducted as part of the Mid-Appalachian Integrated Assessment (MAIA). This is a continuation of sampling initiated in 1993 as part of a Regional EMAP (R-EMAP) project. An additional component of this effort is a pilot study to test protocols for acquiring indicator data from non-wadeable streams and rivers This effort is being implemented for EMAP by EERD in Cincinnati. Data analysis and interpretation activities are shared between EERD and WED-Corvallis.

The second effort is a pilot survey of streams and rivers in Oregon. This is a one-year effort being implemented at WED-Corvallis. Primary objectives are to evaluate existing EMAP sampling and analysis protocols for their suitability in Northwestern streams, and to provide data to make a preliminary assessment of resource conditions. Data will be shared between the plot survey and other studies, such as the Region 10 R-EMAP study and a monitoring effort being conducted by the Oregon Department of Fish and Wildlife. These latter two efforts operate under separate QA project plans, but are using approaches and methods to maximize the comparability of data across all three studies.

1.2.3 Overview of Field Operations

Field data acquisition activities are implemented for both the MAIA survey and the Oregon pilot survey using a similar approach (Table 1), based on guidance developed for earlier EMAP studies (Baker and Merritt 1990). Preparation for a survey may be considered to be initiated with selection of the sampling locations by the Design Team. This is normally completed at least 6 months to one year prior to the planned start of sampling. With the sampling location list, Field Coordinators can begin work on obtaining access permission to each site and necessary scientific collecting permits from State and Federal agencies. Field coordinators also work with indicator researchers and others to coordinate equipment and supply requirements. This helps to ensure comparability of indicator-specific protocols across surveys.

Field measurements and samples are collected by well-trained teams. The number and size of teams depends on the duration of the sampling window, geographic distribution of sampling locations, number and complexity of samples and field measurements, and other

TABLE 1. CRITICAL LOGISTICS ELEMENTS (from Baker and Merritt, 1990)

Logistics Plan Component	Required Elements
Project Management	Overview of Logistic Activities Staffing and Personnel Requirements Communications
Access and Scheduling	Sampling Schedule Site Access Reconnaissance
Safety	Safety Plan Waste Disposal Plan
Procurement and Inventory Control	Equipment, Supplies, and Services Requirements Procurement Methods and Scheduling
Training and Data Collection	Training Program Field Operations Scenario Laboratory Operations Scenarios Quality Assurance Information Management
Assessment of Operations	Field Crew Debriefings Logistics Review and Recommendations

factors. Sampling personnel may be full-time EMAP support staff or temporary hires. In either case, a formal training program is conducted, stressing hands-on practice of methods, comparability among crews, collection of high quality data and samples, and safety.

For each sampling location, a packet is prepared containing, as applicable: road maps, bathymetric maps, copies of written access permission, scientific collection permits, coordinates of the randomly selected index site, a topographic map with the index site location marked, and local area emergency numbers. Whenever possible, team leaders attempt to contact landowners approximately 2 days before the planned sampling date. As the design requires repeat visits to selected sampling locations, it is important for the field teams to do everything possible to maintain good relationships with landowners. This includes prior contacts, respect of special requests, closing gates, minimal site disturbance, and removal of all materials including flagging and trash.

A variety of methods may be used to access a site, including vehicles and boats. Some sampling locations require teams to hike in, transporting all equipment in backpacks. For this reason, ruggedness and weight are important considerations in the selection of equipment and instrumentation (see Section 3.6). Teams may need to camp out at the sampling location and so are equipped with the necessary camping equipment.

The site verification process is shown in Figure 1. Upon arrival at a site, the location is verified by a Global Positioning System (GPS) receiver, landmark references, and/or local residents. Samples and measurements for various indicators are collected in a specified order (Figure 2). This order has been set up to minimize the impact of sampling for one indicator upon subsequent indicators; for example, water chemistry samples from streams are collected before collecting benthic invertebrates as the benthic invertebrate method calls for kicking up sediments. All methods are fully documented in step-by-step procedures in field operations manuals (e.g., Klemm and Lazorchak, 1995). The manuals also contain detailed instructions for completing documentation, labeling samples, any field processing requirements, and sample storage and shipping. Any revision of methods must be approved in advance by the Indicator Lead. Field communications may be through Field Coordinators, regularly scheduled conference calls, a Communications Center, or an electronic mail/bulletin board.

Figure 3 illustrates the flow of sample information and field and laboratory data from collection to an computerized data base. A field portable personal computer (PC), programmed

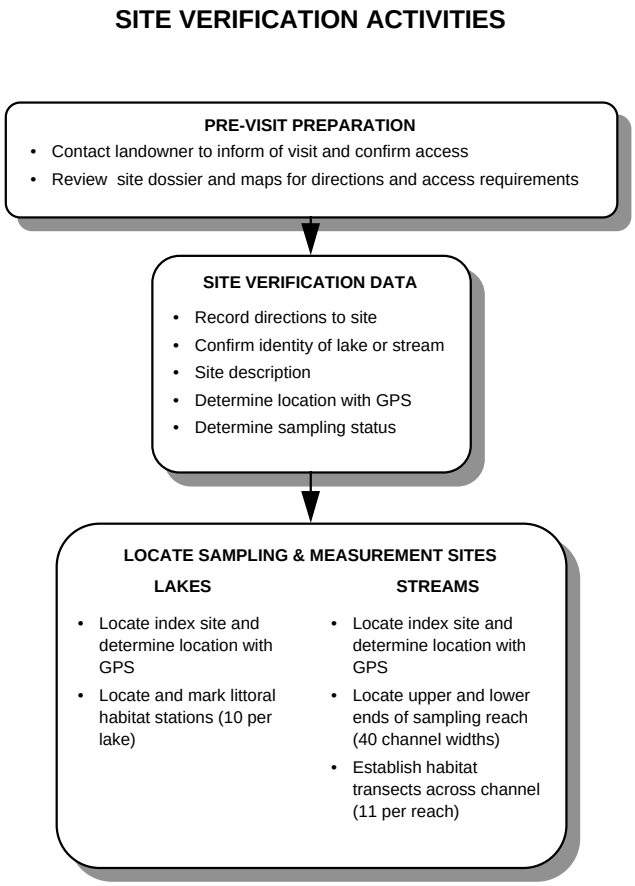

Figure 1. Site verification activities for EMAP surface water field surveys.

SUMMARY OF SAMPLING AND MEASUREMENT ACTIVITIES: STREAMS FIELD CREWS

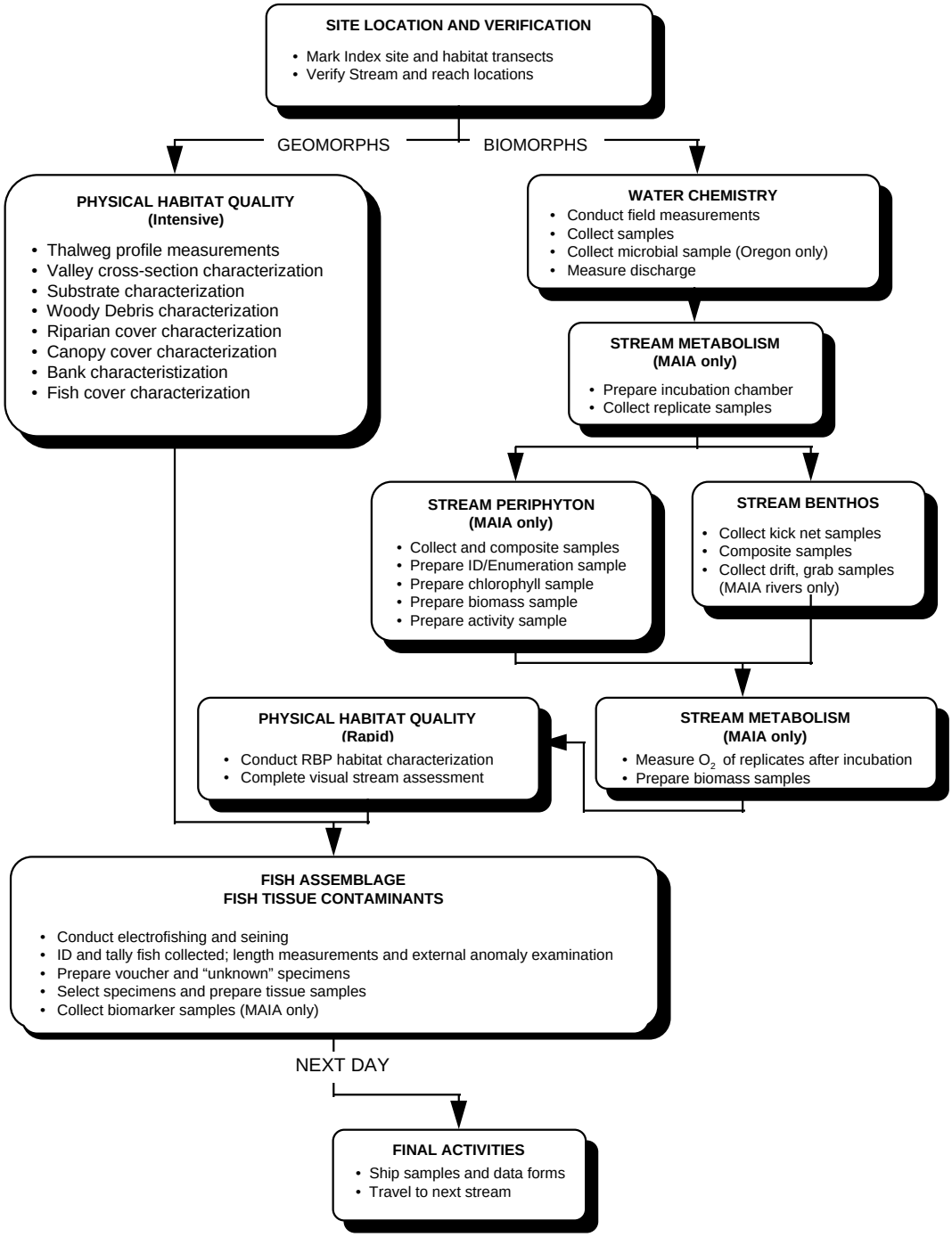

Figure 2. Summary of field activities for EMAP stream and river sampling.

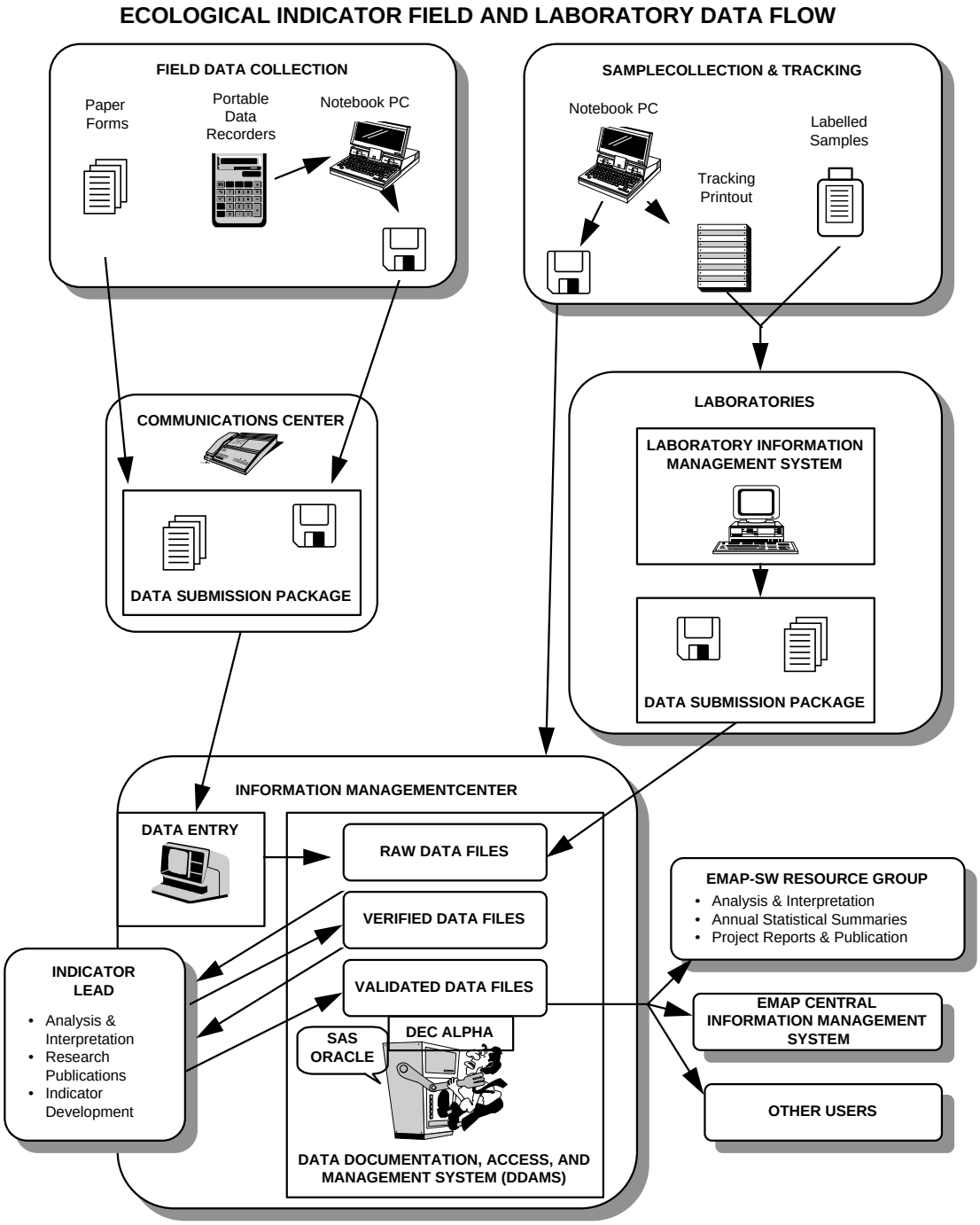

Figure 3. Information and data flow for EMAP surface water research projects.

specifically for use with EMAP surface water research projects, may be used to record all field information. Standardized field forms may be used the primary means of data recording , or as a alternate to the PC in the event of a malfunction. Upon completion, the data input file and/or form is reviewed by a person other than the person who initially entered the information. Prior to departure from the field site, the team leader reviews all forms and labels for completeness and legibility and ensures that all samples are properly labeled and packed. In addition to the documentation required by the EMAP survey, field teams are encouraged to maintain personal logs.

Upon return from a field sampling site (either to the field team's home office or to a motel), completed data forms are sent to the EMAP information management staff at WED for entry into a computerized data base. If field data are recorded electronically, the PC data files are downloaded to disk and also (if possible) transferred electronically to the EMAP information management staff at WED-Corvallis. At WED, electronic data files are reviewed independently to verify that values are consistent with those recorded on the field data form or original field data file (see Section 4.1.4). Samples are stored or packaged for shipment in accordance with instructions contained in the field manual. Samples which must be shipped are delivered to a commercial carrier; copies of bills of lading or other documentation is maintained by the team. The recipient is notified to expect delivery; thus, tracing procedures can be initiated quickly in the event samples are not received. Chain-of-custody forms are completed for all transfers of samples, with copies maintained by the field team.

The field operations phase is completed with collection of all samples or expiration of the sampling window. Following completion of all sampling, a debriefing session will be scheduled (see Table 1). These debriefings cover all aspects of the field program and solicit suggestions for improvements. Experience of prior EMAP projects have shown these debriefings to be invaluable in implementing continuous improvements to EMAP field operations supporting research activities.

1.2.4 Overview of Laboratory Operations

Holding times for EMAP surface water samples vary with the sample types and analytes. Thus, some analytical analyses begin as soon as sampling (e.g., water chemistry) begins while others are not even initiated until sampling has been completed (e.g., benthic invertebrates).

Analytical methods are summarized in the specific indicator sections of this QAPP. In most cases, standard methods are used and are referenced. Where experimental methods are used or standard methods are modified, these methods are documented by the indicator lead in the laboratory methods manual or in internal EMAP documentation, and may be described in standard operating procedures developed by the analytical laboratory.

Chemical, physical, or biological analyses may be performed in-house or by contracted or cooperator laboratories. Laboratories providing analytical support must have the appropriate facilities to properly store and prepare samples, and appropriate instrumentation and staff to provide data of the required quality within the time period dictated by the project. Laboratories are expected to conduct operations using good laboratory practices (Table 2).

All laboratories providing analytical support to EMAP surface waters research projects must adhere to the provisions of this integrated QAPP. Laboratories should provide information documenting their ability to conduct the analyses with the required level of data quality. Such information might include results from interlaboratory comparison studies, analysis of performance evaluation samples, control charts and results of internal QC sample or internal reference sample analyses to document achieved precision, bias, accuracy, and method detection limits. Contracted laboratories may be required to provide copies of standard operating procedures (SOPs). Laboratories may also be required to successfully analyze at least one performance evaluation sample for target analytes before routine samples can be analyzed. Laboratory operations may be evaluated by technical systems audits, performance evaluation studies, and by participation in interlaboratory round-robin programs.

1.2.5. Data Analysis and Reporting

Indicator leads are responsible for development of a data verification and validation strategy. These processes are described in the internal indicator research strategies and summarized in the indicator-specific sections of this QAPP. Validated data are transferred to the central data base (Figure 3) managed by EMAP information management support staff located at WED-Corvallis. Information management activities are discussed further in Section 4. Data in the WED data base are available to Indicator Leads for use in development of indicator metrics. The data may be released externally only with the written permission of the EMAP Director. All validated measurement and indicator data from a particular surface water research project is

TABLE 2. GENERAL GUIDELINES FOR EMAP ANALYTICAL SUPPORT LABORATORIES

- A program of scheduled maintenance of analytical balances, water purification systems, microscopes, laboratory equipment, and instrumentation.
- Verification of the calibration of analytical balances using class "S" weights which are certified by the National Institute of Standards and Technology (NIST).
- Verification of the calibration of top-loading balances using NIST-certified class "P" weights.
- Checking and recording the composition of fresh calibration standards against the previous lot. Acceptable comparisons are ±2 percent of the theoretical value.
- Recording all analytical data in bound logbooks in ink, or on standardized recording forms.
- Monitoring and recording (in a logbook or recording form) temperatures and performance of cold storage areas and freezer units. During periods of sample collection operations, monitoring must be done on a daily basis.
- Verifying the efficiency of fume hoods.
- If needed, having a source of reagent water meeting American Society of Testing and Materials (ASTM) Type I specifications for conductivity (< 1 µS/cm at 25 °C; ASTM 1984) available in sufficient quantity to support analytical operations.
- Labeling all containers used in the laboratory with date prepared, contents, and initials of the individual who prepared the contents.
- Dating and storing all chemicals safely upon receipt. Chemicals are disposed of properly when the expiration date has expired.
- Using a laboratory information management system to track the location and status of any sample received for analysis.
- Reporting results using standard formats and units compatible with the EMAP information management system.

eventually transferred to the EMAP information management system administered at the Atlantic Ecology Division-Narragansett, RI.

2.0 DATA QUALITY OBJECTIVES

It is a policy of the U.S. EPA and its laboratories that Data Quality Objectives (DQOs) be developed for all environmental data collection activities. Data quality objectives are statements that describe the level of uncertainty (both qualitative and quantitative) that can be associated with environmental data without compromising their intended use. Data quality objectives thus provide the criteria to design a sampling program within cost and resource constraints or technology limitations imposed upon a project or study.

2.1 Data Quality Objectives for EMAP Surface Water Research Activities

The DQOs established as program-level goals by EMAP are applicable to surface water-related research projects. Target criteria established by EMAP for estimating status and trends in condition are as follows:

- Estimate the status of a population of resources (the proportion of the population that is at or below some value of concern for an indicator) with 95 percent confidence intervals that are within ±10 percent of the estimate.

- Determine an average change in condition of a resource population (estimated as the change in the proportion of the population that is at or below some value of concern for an indicator) of twenty percent over 10 years with 95 percent confidence and a statistical power of 0.8.

However, these DQOs cannot be achieved, nor can it be known whether they are achievable, until indicators are fully developed and the sampling design is optimized. Progress towards full implementation of routine surface water monitoring activities within EMAP requires data and other information needed to make decisions regarding the refinement of the overall sampling design and to evaluate proposed indicators of ecological condition. Estimates of the magnitude of various sources of natural and extraneous variation are needed to refine the basic sampling design with respect to the number of sampling sites required and the frequency and number of repeat sampling visits needed within or among years, regardless of the number or types of different indicators being used.

For many of the indicators, little information is available on the components of variability and their magnitude, especially as they might vary among geographic regions. As a first step in developing DQOs, pilot and demonstration surveys are designed to provide information on the sources of variability and their relative magnitude. This is done through index and overall sampling designs, which include revisit and repeat sampling, multiple sampling locations within a site, sample compositing, use of performance evaluation (PE) samples, and other means of obtaining estimates of variability components. Within each indicator, performance objectives are established for all measurements based on the level of quality required by individual indicator leads to develop and evaluate indicator metrics (combinations of one or more measurements into a new variable). Initial performance objectives are set based on the best estimate of the quality of individual measurements needed to produce rigorous regional population estimates and discern trends. These performance objectives are referred to as measurement quality objectives (MQOs). MQOs are expressed in terms of such data quality attributes as precision, accuracy or bias, taxonomic accuracy, completeness, comparability, representativeness, and method detection limits, as applicable.

The indicator evaluation activities conducted in the pilot and demonstration surveys represent a compromise between providing information needed to refine the overall sampling design and that required to develop an indicator that meets the criteria for EMAP implementation. Table 3 presents the criteria against which all potential indicators are evaluated at each stage of their development and eventual implementation. The criteria are both qualitative and quantitative in nature, and the determination of attainment of each criterion is achieved by consensus of indicator leads, program management, and scientific peer reviewers. It is anticipated that some or all of these criteria will become more quantitative as input from potential clients is utilized, or until benchmarks can be developed based on existing indicators that have been implemented and found to be successful.

Once the sources of the greatest variability are identified, they may be minimized through index and overall sampling design changes, which include optimizing the frequency of sampling both within and among sampling locations, use of PE and other QA/QC samples, and implementation of QC procedures. Through these processes, the MQOs may also be refined. Initial DQOs for the indicator or index level may be developed through error propagation techniques. The magnitude of errors propagated from measurements through metrics to an

TABLE 3. GENERAL CRITERIA FOR EVALUATING ECOLOGICAL INDICATORS (from Barber, 1994)

Candidate Indicators:
• Potential or demonstrated importance in assessing status and trends in the ecological conditions of a resource class.
• Provides conceptual linkage of environmental stressors to assessment endpoints or environmental values.
• Potentially capable of responding over gradients of stressor intensity.
• Potentially adaptable to index sampling approach and constraints.
• Sampling and analytical methodologies available and mostly standardized, or have the potential to be successfully adapted to index sampling approach.
• The potential to obtain valid measurements and samples from every resource site is high.
• Additional testing can be accomplished at reasonable cost.
• Information obtained from indicator is not redundant with other indicators.
Core Indicators:
• Demonstrated ability to be implemented on a regional scale as part of an integrated monitoring activity during the index period.
• New information is provided at a regional scale that is not available as part of other existing monitoring programs.
• The magnitude of spatial and temporal variation within each resource site during the index period is small relative to the variation among resource sites.

indicator cannot be understood or estimated until the data are available to develop potential metrics and subject them to sensitivity analyses. In addition, the error distributions of metrics and indicators may not be typical and thus subject to standard techniques for estimation and inference, much like diversity indices or indices of niche breadth and overlap that are utilized in community ecology. As the available data base increases through the full 4-year sampling cycle and additional regions are sampled, additional refinement of the DQOs is made possible. Ultimately, index or program level DQOs may be developed which may be comparable to the EMAP program-level DQOs.

2.2 Attributes of Data Quality

Based on the currently perceived data quality requirements for each indicator research program, acceptance criteria for measurement data are defined for several attributes of data quality, described in the following sections. These criteria are established based on consideration of important sources of error (if known). For each ecological indicator being evaluated for EMAP, performance objectives are defined to control and evaluate measurement error attributable to the collection and analysis of samples or data. As performance data become available to evaluate error at levels above the measurement level (e.g., indicator or endpoint), additional performance objectives will be defined.

For each indicator measurement program, performance objectives (associated primarily with measurement error) are established for several different attributes of data quality (following Smith et al., 1988). Specific objectives for each indicator are presented in the indicator sections contained in part II of this QAPP. The following sections define the data quality attributes and present approaches for evaluating them against acceptance criteria established for the program.

2.2.1 Method Detection Limits

For chemical measurements, requirements for the method detection limit (MDL) are established. The MDL is defined as the lowest level of analyte that can be distinguished from zero with 99 percent confidence based on a single measurement (Glaser et al., 1981). The MDL for an individual analyte is calculated as:

$$MDL \quad t_{[á \quad 0.01,\ í \quad n\ 1]} \times s \qquad (1)$$

where *t* is a Students' *t* value at a significance level (á) of 0.01 and n-1 degrees of freedom (í), and *s* is the standard deviation of a set of *n* measurements of a standard solution. The standard contains analyte concentrations between two and three times the MDL objective, and is subjected to the entire analytical method (including any preparation or processing stages). At least seven nonconsecutive replicate measurements are required to calculate a valid estimate of the MDL. Replicate analyses of the standard should be conducted over a period of several days (or several different calibration curves) to obtain a long-term (among-batch) estimate of the MDL.

Laboratories should periodically monitor MDLs on a per batch basis. Suggested procedures for monitoring MDLs are: (1) to analyze a set of serial dilutions of a low level standard, determining the lowest dilution that produces a detectable response; and (2) repeated analysis (at least seven measurements) of a low-level standard within a single batch.

Estimates of MDLs (and how they are determined) are required to be submitted with analytical results. Analytical results associated with MDLs that exceed the detection limit objectives are flagged as being associated with an unacceptable MDL. Analytical data that are below the estimated MDL are reported, but are flagged as being below the MDL.

2.2.2 Precision, Bias, and Accuracy

Precision and bias are estimates of random and systematic error in a measurement process (Kirchmer, 1983; Hunt and Wilson, 1986). Collectively, precision and bias provide an estimate of the total error or uncertainty associated with an individual measurement or set of measurements. Systematic errors are minimized by using validated methodologies and standardized procedures. Precision is estimated from repeated measurements of samples. Net bias is determined from repeated measurements of solutions of known composition, or from the analysis of samples that have been fortified by the addition of a known quantity of analyte. For analytes with large ranges of expected concentrations, objectives for precision and bias are established in both absolute and relative terms, following the approach outlined in Hunt and Wilson, 1983. At lower concentrations, objectives are specified in absolute terms. At higher concentrations, objectives are stated in relative terms. The point of transition between an absolute and relative objectives is calculated as the quotient of the absolute objective divided by the relative objective (expressed as a proportion, e.g., 0.10 rather than as a percentage, e.g., 10%).

Precision in absolute terms is estimated as the sample standard deviation when the number of measurements is greater than two:

$$s \quad \sqrt{\frac{\mathbf{j}(x_i \quad \bar{X})^2}{(n \quad 1)}} \qquad (2)$$

where x_i is an individual measurement, $\bar{X}$ is the mean of the set of measurements, and n is the number of measurements. Relative precision for such measurements is estimated as the relative standard deviation (RSD, or coefficient of variation, [CV]):

$$RSD \quad \frac{s}{\bar{X}} \times 100 \tag{3}$$

where s is the sample standard deviation of the set of measurements, and $\bar{X}$ equals the mean value for the set of measurements.

Precision based on duplicate measurements is estimated based on the range of measured values (which equals the difference for two measurements). At higher concentrations, the relative percent difference (RPD) is calculated as:

$$RPD \quad \frac{|x_1 - x_2|}{\bar{X}} \times 100 \tag{4}$$

where x_1 is the first measured value, x_2 is the second measured value, and $\bar{X}$ is the mean value of the two sample measurements. Precision objectives based on the range of duplicate measurements can be calculated as:

$$Critical\ Range \quad s \times \sqrt{2} \tag{5}$$

where s represents the precision objective in terms of a standard deviation. Range-based objectives are calculated in relative terms as:

$$Critical\ RPD \quad RSD \times \sqrt{2} \tag{6}$$

where *RSD* represents the precision objectives in terms of a relative standard deviation.

For repeated measurements of samples of known composition, net bias (B) is estimated in absolute terms as:

$$B \quad \bar{X} \quad T \tag{7}$$

where $\bar{X}$ equals the mean value for the set of measurements, and T equals the theoretical or target value of a performance evaluation sample. Bias in relative terms ($B[\%]$) is calculated as:

$$B(\%) \quad \frac{\bar{X} \quad T}{T} \times 100 \tag{8}$$

where $\bar{X}$ equals the mean value for the set of measurements, and T equals the theoretical or target value of a performance evaluation sample.

Accuracy is estimated for some analytes from fortified or spiked samples as the percent recovery. Percent recovery is calculated as:

$$\%\ recovery \quad \frac{C_{i\ s} \quad C_i}{C_s} \times 100 \tag{9}$$

where $C_{i\ s}$ is the measured concentration of the spiked sample, C_i is the concentration of the unspiked sample, and C_s is the concentration of the spike.

2.2.3 Taxonomic Accuracy

There are two equations used to estimate taxonomic accuracy in EMAP surface water-related research projects. The first method applies to those indicators that require the identification and subsequent enumeration of organisms (e.g., benthic invertebrates); the second applies to those indicators for which identification is verified by taxonomic experts, but which lack a means of verifying field enumerations (e.g., fish assemblage). For either method, requirements for this data quality attribute include: (1) the specification of the required taxon level (e.g., family, genus, or species); and (2) the specification of appropriate taxonomic reference material (e.g., identification keys, systematic references, standards for nomenclature, and voucher specimen collections).

Taxonomic accuracy is controlled and evaluated by conducting independent identifications of a subset of samples. The independent check is conducted by an experienced taxonomist, whose identifications are accepted as the "true" value for the sample. In addition, sample residuals are examined to check the accuracy of the original enumeration. A tally is

maintained of any organisms found. Overall accuracy in identifications is estimated with the approach developed for the Estuaries research activities conducted by EMAP:

$$Accuracy(\%) \quad \frac{N_t \quad (n_i \quad {}^{*}n_c{}^{*})}{N_t} \times 100 \tag{10}$$

where N_t is the sum of the number of specimens counted in the original sample and the number of additional specimens found during the repeat enumeration, n_i is the number of specimens incorrectly identified in the initial analysis, and n_c is the number of specimens that were miscounted in the original analysis. If there is no means to perform the enumeration check needed to use equation 9, taxonomic accuracy may be estimated by using:

$$Accuracy(\%) \quad \frac{N_t \quad n_i}{N_t} \times 100 \tag{11}$$

where N_t is the total number of voucher specimens in the group or batch examined by the taxonomic expert and n_i is the number of specimens that were originally misidentified.

Taxonomic similarity is a estimation of taxonomic accuracy generated by separate identification of split samples. This technique is valid only for biological samples which are of sufficient size and homogeneity to reasonably ensure that the splits are equivalent (e.g., periphyton). Percent similarity (PS) is estimated according to Whittaker (1975):

$$PS(\%) \quad 1 \quad 0.5 \; \mathbf{j}^{*}p_a \; p_b{}^{*} \times 100 \tag{12}$$

where p_a is a decimal importance value for a given species in sample split “A” and p_b is the decimal importance value for the same species in sample split “B”.

2.2.4 Completeness

Completeness requirements are established and evaluated from two perspectives. First, valid data for individual indicators must be acquired from a minimum number of sampling locations in order to make subpopulation estimates with a specified level of confidence or sampling precision. This objective is generally 50 sites, with an absolute minimum of 30 sites. For sites that are revisited within a single year and/or across years, the objective is to have not more than one site "lost", or to acquire valid data from at least 90 percent of these sites, whichever criterion is larger at a particular sample size.

Within each indicator, completeness objectives are also established for individual samples or individual measurement variables or analytes. These objectives are estimated as the percentage of valid data obtained versus the amount of data expected based on the number of samples collected or number of measurements conducted. Where necessary, supplementary objectives for completeness are presented in the indicator-specific sections of this QAPP.

2.2.5 Comparability

Comparability is defined as the confidence with which one data set can be compared to another (Stanley and Verner, 1985; Smith et al., 1988). Comparability criteria for surface water research projects in EMAP are given in Table 4. For all indicators, comparability is addressed by the use of standardized sampling procedures and analytical methodologies by all sampling crews and laboratories. Comparability of data within and among indicators is also facilitated by the implementation of standardized quality assurance and quality control techniques and standardized performance and acceptance criteria. For all measurements, reporting units and format are specified, incorporated into standardized data recording forms, and documented in the information management system. Comparability is also addressed by providing results of QA sample data, such as estimates of precision and bias, conducting methods comparison studies when necessary, and conducting interlaboratory performance evaluation studies among EMAP

TABLE 4. COMPARABILITY CRITERIA

Criterion	Evaluation and Assessment
Comparability of EMAP SURFACE water data collected in a single year for an individual research project	Identical protocols and methods used by all field crews and laboratories
Comparability of EMAP surface water data to related projects in a single year (TIME, R-EMAP	Consistent reporting of data (units, taxonomic nomenclature)
Comparability of EMAP surface water data to EMAP, R-EMAP, and TIME data collected in previous years	Consistent reporting of data (units, level of effort, standardized taxonomic nomenclature)
	Comparison of index period and annual variance estimates and PE sample results

support laboratories. These latter activities allow for comparability to be addressed through time or by external data users. Comparability of performance between EMAP support laboratories and other laboratories is addressed by the participation of laboratories in interlaboratory comparison studies, such as those conducted by the U.S. Geological Survey and the National Water Research Institute of Canada.

In order to provide estimates of trends in indicators related to the societal values, data collected each year must be comparable to data collected in previous and succeeding years. Data from EMAP regional survey sites must be comparable to data collected from R-EMAP sites within the same geographic area to provide sufficient sample size and regional representativeness to address the objectives of R-EMAP. Quantitative estimates of comparability are obtained through comparison of within and among-year estimates of variance components from replicate samples, and, where applicable, through comparison of precision and bias estimates obtained from PE sample analyses.

2.2.6 Representativeness

Representativeness is defined as "the degree to which the data accurately and precisely represent a characteristic of a population parameter, variation of a property, a process characteristic, or an operational condition" (Stanley and Verner, 1985, Smith et al., 1988). At

one level, representativeness is affected by problems in any or all of the other attributes of data quality.

At another level, representativeness is affected by the selection of the target surface water bodies, the location of sampling sites within that body, the time period when samples are collected, and the time period when samples are analyzed. The probability-based sampling design should provide estimates of condition of surface water resource populations that are representative of the region. The individual sampling programs defined for each indicator attempt to address representativeness within the constraints of the sampling design and index sampling period. Holding time requirements for analyses ensure analytical results are representative of conditions at the time of sampling. Use of QA and quality control (QC) samples which are similar in composition to samples being measured provides estimates of precision and bias that are applicable to sample measurements.

3.0 MEASUREMENT AND DATA ACQUISITION

The overall sampling program for EMAP surface water research projects requires a probability-based scheme for selecting surface water bodies where sampling activities are conducted. Superimposed on the basic probability sample design for selection of locations to be sampled are various designs to provide estimates of important sources of spatial and temporal variability in the various indicators being implemented. Details regarding the specific application of the EMAP design to surface waters resources are described in Paulsen et al. (1991) and Stevens (1994). The specific details for the collection of samples associated with different indicators are described in the indicator-specific sections of this QAPP.

3.1 Probability Based Sampling Design and Site Selection

Sites are selected for each EMAP surface water survey, beginning with the first pilot conducted in 1991, by using a two-stage process employing a systematic grid of sampling points developed for use by all EMAP resource groups (Overton et al., 1991). The selection process is automated, utilizing digital maps and geographic information system (GIS) techniques and equipment (Selle et al., 1991).

Quality assurance for GIS methodologies is focused on aspects of accuracy (e.g., how well do digitized maps provide information of what is actually present at a location) and the representativeness of this information. Three basic types of errors have been identified by the EMAP design group:

- Map-related errors: These are errors due to inconsistencies between different types (or scales) of maps (e.g., paper maps versus digitized versions).
- Landscape-related errors: These are errors due to changes occurring at a site since the corresponding map was last revised. Such changes could be natural (e.g., a lake converting to a wetland due to natural successional processes) or anthropogenic (e.g., damming a stream to create a new reservoir).
- Other errors: Software developed for digitizing maps or other associated GIS processing applications may introduce errors.

The GIS staff at WED that support surface waters research in EMAP have developed quality control (QC) procedures for controlling some of these errors. Other types of errors are quantified as they are discovered, essentially by using ground truthing as a standard for comparison.

Figure 4 summarizes the probability-based selection process. Lake, reservoir, stream, and wetlands resource information is initially derived from hydrologic information which is part of U.S. Geological Survey (USGS) 1:100,000 scale digital line graphs (DLGs). Specific spatial information associated with surface water bodies (e.g., geographic coordinates and surface area or stream "blue line" length) are extracted from the DLGs into a data base file. The accuracy and completeness of the extraction process is monitored by checking the spatial file for the inclusion of larger lakes and reservoirs (> 10 ha) and streams (3rd order and higher) that were present on the "parent" DLGs. Missing surface water bodies are added to the spatial file.

The first stage of the probability sample (termed the "Tier I" sample) is developed by intersecting the spatial file of surface water body information with a second file containing spatial information related to the EMAP systematic sampling grid. This information includes locational information regarding the sampling points on the grid and an associated 40-km2 hexagon area centered on each sampling point. The Tier I sample represents all surface water bodies whose digitized labeling points are located within the boundaries of one of the hexagons.

A quality control check is made by comparing a selected subset of the Tier I sample against the parent DLGS. Any noted discrepancies are reconciled by using the corresponding paper topographic maps. Error rates for the frame are extrapolated from the error rates found in the Tier I sample.

The second stage of site selection involves selecting a subset of the Tier I sample. This subset (termed the "Tier II" sample), represents sites that are expected to be visited by field sampling crews. The Tier II sample is selected through a process that incorporates the desired Tier II sample size and any Tier I stratification needed (e.g, lake area, stream order). Sites are selected randomly from the Tier I sample, with the constraint that the spatial distribution of sites be preserved. Each Tier II site has an associated inclusion probability with which any measured attribute can be related to the target population of sites.

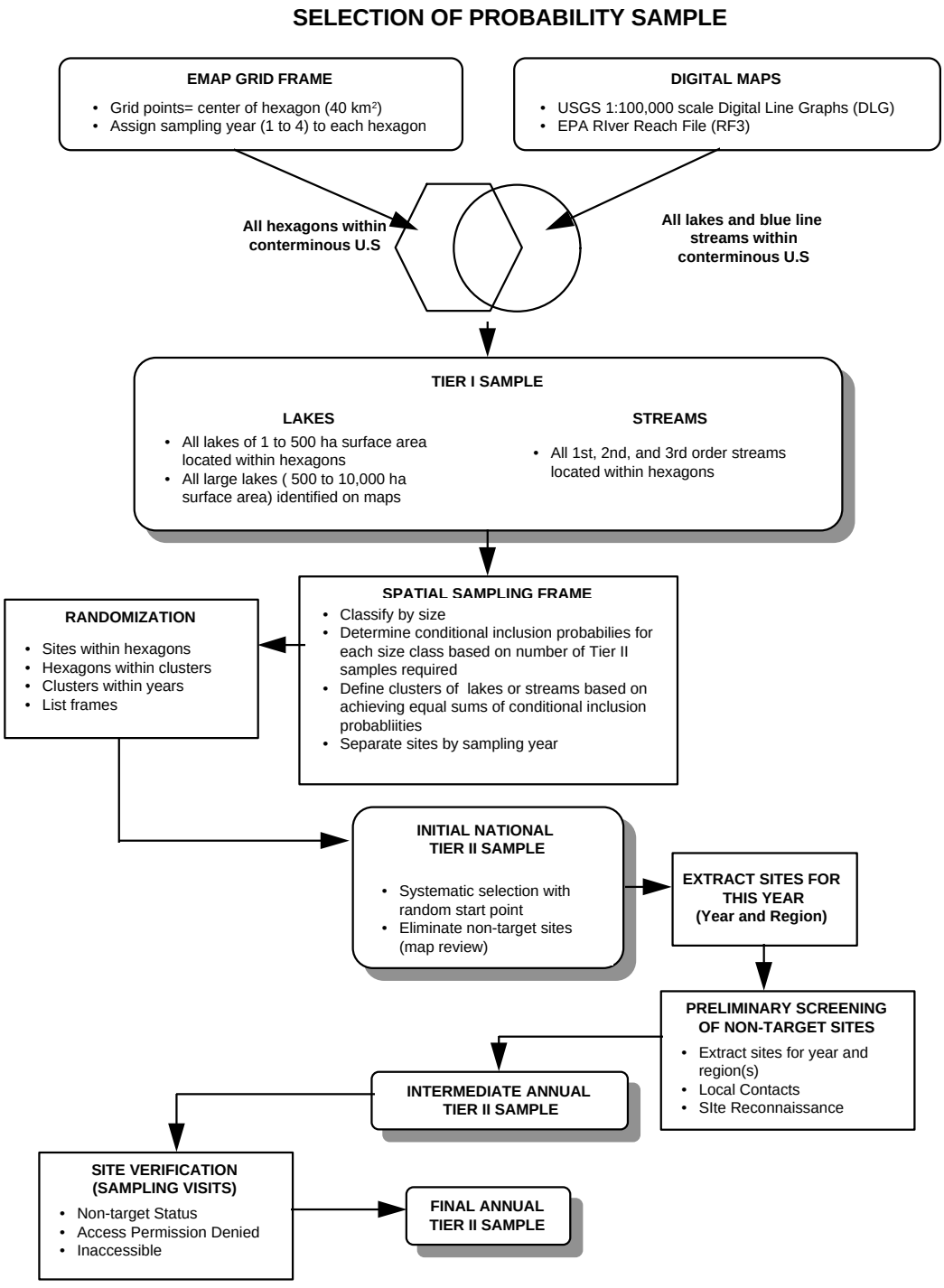

Figure 4. Selection of probability-based sampling locations for EMAP surface water research activities.

A sample size of at least 50 (minimum=30) is necessary for making statements about the condition of a regional subpopulation with reasonable precision. Larger total sample sizes are necessary if the condition of numerous subpopulations are to be described. Overselection should protect against a reduction in sample size due to: (1) landscape-related errors not portrayed by the DLGs, (2) the inability to visit a site due to weather conditions or lack of access permission, or (3) the reclassification of a site to nontarget status when it is visited.

3.2 Site Selection For Associated Programs

The selection of sites for associated sampling programs (e.g., TIME, R-EMAP) is accomplished using basically the same procedure as used to develop the Tier II sample for EMAP surface water surveys, although in some cases the site selection may be non-random (e.g., for special-interest studies). All sites selected for the EMAP surface water surveys also satisfy the target population criteria for the TIME and R-EMAP projects. A Tier II level sample is developed by applying the augmented grid to certain regions (e.g., high-elevation regions known to be subject to acidic deposition) and selecting the desired number of additional sites. Quality assurance and QC procedures developed for the EMAP sampling design and site selection are also applicable to the TIME and R-EMAP projects.

3.3 Variance Components

Interpretations of regional patterns in the condition of surface water resources is predicated on the use of data from a single sampling location during a specified "index period." Several components of variance (Table 5) are estimated using a program of replicated sampling. These results are then used to refine future sampling designs and strategies to minimize the effects of those components having the largest variance.

The replicate sampling strategy is currently based on a factorial design (Larsen et al., 1995). Of particular interest for the pilot and demonstration phases is the estimation of $ó^2_{year}$ and $ó^2_{index}$. These two components appear to have the most influence on the capability to detect trends and estimate status, respectively. Index variance is composed of temporal variance within a sampling period confounded with measurement error of various types. If the magnitude of

TABLE 5. IMPORTANT VARIANCE COMPONENTS FOR EMAP SURFACE WATERS RESEARCH PROJECTS (from Larsen et al. 1995)

Variance Component	Description
	Population or Design-related Components
Population ($ó^2_{pop}$)	Variance associated with extrapolation from probability sample to entire target population. Function of number of probability samples in population or subpopulation of interest
Extraneous variance components (estimated from a subset of sites visited within and across years)	
Site ($ó^2_{site}$)	Observed variance among all sites or streams sampled over multiple-year sampling cycle
Year ($ó^2_{year}$)	Coherent variability affecting all sites equally, due to regional-scale factors such as climate or hydrology
Site × year interaction ($ó^2_{site*year}$)	Variation observed at individual sites above coherent variation
Residual ($ó^2_{residualr}$)	Includes temporal variation at a single site within a single index period confounded with "measurement error" due to sources of field and laboratory error

index error is sufficiently large to impact status estimates, then various components of measurement error are investigated to determine if any reduction in magnitude will be of benefit.

3.4 Sampling Locations And Selection Methods

Sections 3.1 through 3.3 describe the process used to select sampling locations for the Tier II sample, for associated sampling projects, and for estimating particular components of variability. The results of this process for the surveys to be conducted this year are presented in Figure 5. Lists of sampling location names and coordinates are contained in the field operations manuals and the "design" data base..

Sampling for every indicator is not necessarily conducted in all EMAP surface water research projects or associated projects. The objectives of different projects may be slightly different such that certain indicators are not needed. Within an individual research project, data for individual indicators may only be collected at certain sampling locations . The availability of data on aspects of temporal, spatial, and measurement variability may preclude the need to

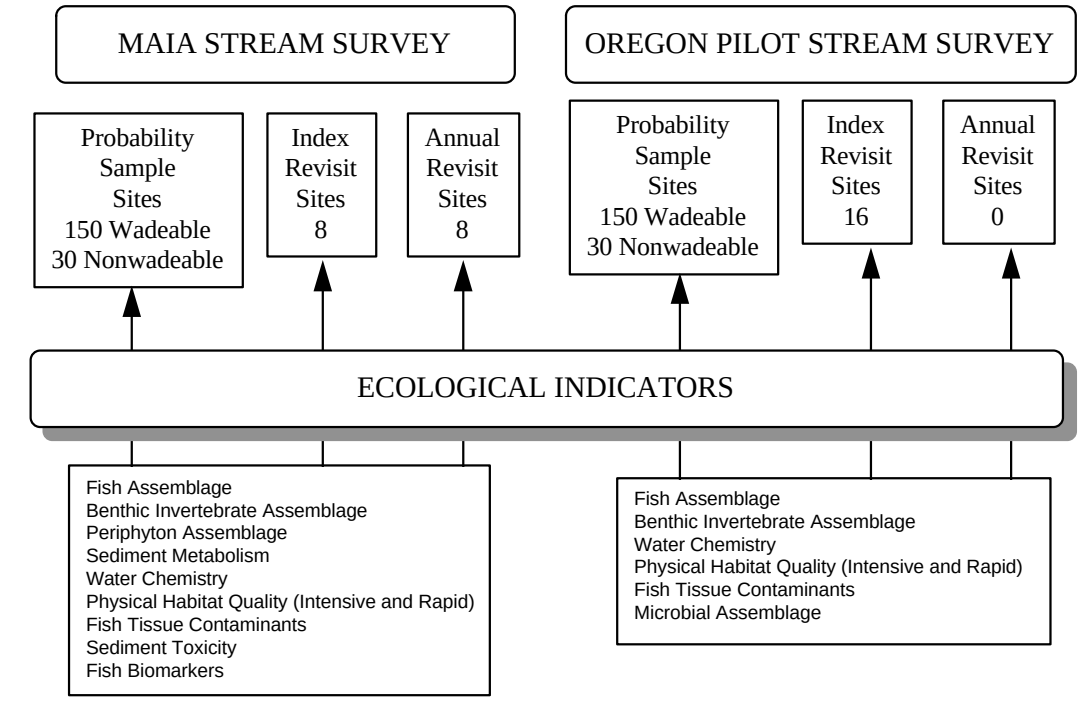

Figure 5. Sampling plan for EMAP surface water research projects.

sample for certain indicators on repeat visits. Time, cost, and data needs may dictate use of an abbreviated or simplified sampling procedure for certain sites, while intensive sampling is conducted at others to provide data for special interest studies. Figure 5 also illustrates the sampling plan for various ecological indicators for each research project.

3.5 Indicators

The indicators being evaluated in EMAP surface waters research surveys are in various stages of development. For each indicator, standardized sample collection and measurement protocols are developed either from the published literature or from published methods approval organizations such as APHA and ASTM. These protocols are updated as necessary by the indicator leads as the results from monitoring studies are analyzed.

Quality assurance and quality control activities for each indicator research program are developed and compiled in Part II of this QAPP. These descriptions are presented in a consistent format across indicators. For each indicator, there is an introductory section that describes the indicator, long-term research objectives, and relationship to historical monitoring programs, if applicable. The questions to be addressed or hypotheses to be tested in this year's monitoring are provided, if available. Also, if available, the data analysis plan is briefly described. A sampling design section describes the design used at a single site to acquire an index sample; and the overall sampling design (i.e., which indicators are sampled at which site types). A sampling and analytical methods section provides a brief description and/or reference for the sampling and analytical methodologies; the user is referred to the field and laboratory manuals and/or reference for the sampling and analytical methodologies; the user is referred to the field and laboratory manuals and/or cited references for detailed sampling and analytical procedure descriptions. The data quality objectives section provides the measurement quality objectives or data quality objectives in terms of precision, accuracy or bias, completeness, comparability, representativeness, and method detection limit, as applicable to the indicator measurements. The next two sections describe the quality control procedures for the field and laboratory, respectively. These sections describe the QA/QC samples and QC procedures used to ensure the collection of high quality samples and data.

The format used is designed to facilitate documentation of indicator development. These sections are reviewed and updated by the indicator leads on an annual basis. Additionally, this

format is designed to facilitate distribution, in that only the applicable indicator sections need be included in the distribution to specific groups (for example, streams field teams need only receive the sections for indicators sampled in streams). Finally, this format is designed to facilitate the addition of new indicators and deletion of others as the EMAP surface waters research and monitoring activities become fully operational. For these reasons, the individual sections are numbered internally, but are not assigned an overall section number. Instead, the header block on each page identifies the indicator by name, thus permitting rapid location of the sections of interest to the user.

Each indicator is being developed at its own pace. Table 6 is provided the current status of the indicator (candidate or core) and the QA category, following the scheme proposed by Simes (1991). In general, the QA category relates to the degree of development of the individual indicator QA program. Thus, a section for a Category II indicator can be expected to be more detailed than a section for a Category III indicator. As indicators move from candidate to core status, it is expected that the QA category will change from IV or III to II or I and that this will be reflected in the detail and completeness of the indicator QA plan section.

3.6 Quality Control used in the Laboratory and Field

A wide array of equipment and instrumentation is used in the collection, processing, and analysis of EMAP surface water samples. This section describes the general procedures used within to select, test, maintain, and calibrate equipment. Complete equipment lists and instrument-specific calibration procedures are included in the field operations manuals, standard methods, and/or standard operating procedures. Automated data processing (ADP) equipment is not covered in this section. Other aspects of ADP equipment use in EMAP surface water research activities is treated in Section 4.0.

3.6.1 Equipment Selection

The first step in selection of equipment is definition of the required equipment specifications. Most standard methods list the required specifications for all critical instruments

TABLE 6. DEVELOPMENTAL PHASE OF QA PROGRAMS: EMAP SURFACE WATERS INDICATORS

Indicator	Media	Indicator Type	Societal Value	Status	QA Category
Sediment Diatoms	Lakes	Condition	Biological Integrity, Trophic State	Core	II
Fish Assemblage	Lakes, Streams	Condition	Biological Integrity, Fishability	Candidate	III
Zooplankton	Lakes	Condition	Biological Integrity, Fishability	Candidate	III
Benthic Macroinvertebrate Assemblage	Lakes, Streams	Condition	Biological Integrity, Trophic State	Candidate	III
Bird Assemblage	Lakes	Condition	Biological Integrity	Candidate	III
Periphyton Assemblage	Streams	Condition	Biological Integrity, Trophic State	Candidate	III
Sediment Metabolism	Streams	Stressor	Biological Integrity, Trophic State	Candidate	III
Microbial Assemblage	Streams	Condition/Stressor	Biological Integrity, Trophic State	Research	IV
Water Chemistry	Lakes, Streams	Stressor	Trophic State	Core	II
Physical Habitat	Lakes, Streams	Condition, Stressor	Biological Integrity, Trophic State, Fishability	Candidate	III
Sediment Toxicity	Streams	Condition	Biological Integrity, Fishability	Candidate	III
Fish Tissue	Lakes, Streams	Stressor	Biological Integrity, Fishability	Candidate	II
Fish Biomarkers	Streams	Stressor	Biological Integrity	Research	IV

and equipment. The particular circumstances of the activity may dictate additional specifications (for example, all field equipment which is transported by backpack must be rugged and lightweight in addition to meeting specifications for precision and accuracy). Where specifications are not available in the method, they are determined by the indicator lead and may be based on previous experience with the method, the particular needs of EMAP, and consultations with other experts. Specifications may include (but are not limited to) such criteria as: precision, accuracy, sensitivity, threshold (detection limit), repeatability, ease of use and maintenance, ruggedness, weight, power requirements, operational range, reliability, watertightness, applicable temperature range, safety, and cost. Individual specifications criteria may be prioritized or grouped as critical, desirable options, and tie-breakers, if necessary.

3.6.2 Equipment Procurement

Instrumentation and equipment already available to EMAP from participating organizations are used whenever possible (e.g., U. S. Fish and Wildlife boats, EPA equipment used in previous acid ran studies). Besides being cost-effective, is advantageous to use existing equipment because the performance history under EMAP field and laboratory conditions is known, and support personnel are familiar with its use, care, and maintenance. If the instrumentation or equipment is old, reconditioning and factory overhaul and calibrations should be considered. At a minimum it is necessary to check with the manufacturer to ensure that parts and service are still available for that particular model.

If available equipment cannot be located, a vendor survey is conducted. With very few exceptions, all equipment used in EMAP surface water research is available off-the-shelf. In conjunction with the vendor survey, queries may be made to other users of that equipment, particularly in regard to the more subjective specifications (i.e., ease of use and maintenance, reliability). In many cases, the vendor survey is all that is needed to complete the equipment selection. Where several models appear to meet the specifications or there are remaining questions about the ability of the tentatively selected model to meet the specifications, performance and/or comparison testing may be done, as described below.

In the special case of equipment or use of equipment provided under a contract (e.g., analytical services contracts), the request for proposal (RFP) should request a listing of all critical equipment in the proposal and include evaluation criteria related to that equipment. If alternate

or custom equipment is included in a prospective contractor's proposal, then performance data for that equipment should be requested. Rarely, EMAP may require customized equipment to be developed. If such equipment is to be purchased by the government, then the specifications are to form the basis of the RFP.

3.6.3 Performance And Acceptance Testing

Specific experiments designed to yield information related to the equipment specifications may be conducted with one or with several different equipment models. With one model, this performance testing may be designed strictly as a pass/fail to determine if the model meets the required specifications. With several models, the performance testing maybe conducted as a comparison, with a predetermined ranking or scoring system use to "grade" results. The experiments and the scoring system should be designed to ensure that the greatest weight or a pass/fail grade is given to the highest priority criteria. Lower-priority criteria may be tested as discriminators, to aid in final selection among multiple acceptable candidates.

Once equipment has been selected and procured, a modified version of the performance test may be used as an acceptance test. The acceptance test includes simple inspection of equipment upon arrival to determine that the instrument is not damaged or defective. Additional acceptance testing may include experiments designed to test the ability of the particular unit to meet the manufactures's stated specifications and/or to determine the comparability of multiple units of the same instrument. The level of acceptance testing needed is determined by the criticality of the equipment in terms of resultant sample or data quality, intended use and lifespan of the equipment, previous experience with the manufacturer or instrumentation type, or need to develop instrument-specific procedures

3.6.4 Equipment Maintenance

There are two goals of an equipment maintenance program: 1) to keep equipment in proper working order (and, hence, help to ensure sample or data quality), and 2) to minimize costly "downtime". Before field activities are initiated, all equipment is checked and repaired, serviced, or replaced as necessary. Spare units are maintained in working order to provide quick "swapout" for lost, damaged, or malfunctioning equipment. Alternately, service agreement may

be used which provide for quick repair turnaround and/or equipment loans. In the case of analytical laboratory instrumentation, agreement with other labs or other contingency plans may be developed to ensure completion of sample analysis within specified holding times in the event of an instrument malfunction.

Parts deemed most likely to fail are identified and stocked. Additionally or alternately, agreements may be made with manufacturers or vendors to provide for quick (overnight or two-day) supply of critical parts. In addition, a preventative maintenance program may be developed which recommends replacement of certain components prior to the end of their expected life expectancies. Sources of information on equipment and specific component reliability may be obtained from the manufacturer, vendor, other users of the equipment, and experience. Field team leaders or coordinators and analytical personnel are encouraged to keep records of equipment problems symptoms and causes, components replaced, and troubleshooting attempts. These records and procurement records provide a valuable history in developing and refining the preventative maintenance program.

Specific maintenance procedures are detailed in field operations manuals, standard methods, and standard operating procedures. Summaries of maintenance programs for each of the EMAP surface water indicators is given in the indicator-specific sections of this QAPP.

3.6.5 Equipment Calibration

Calibration is the establishment of a relationship between a standard and a scale reading on a meter or other device or the correct value for each setting of a control knob. Therefore, calibrations is related to accuracy or bias. There are several types of calibration that may be applicable to equipment used in EMAP surface water research activities. These are: 1) factory calibration, 2) electronic calibration, and 3) calibration against know standards. Each of these types is discussed below.

Factory calibrations generally indicate that the instrument has no mechanism for customer adjustment, although it may have a means to set a zero offset. For these instruments, the user may only check the accuracy of the calibration by using calibration or quality check standards. If the instrument fails to meet the established acceptance window, the instrument must be returned to the manufacturer or vendor for adjustment.

Electronic calibration indicates that the instrument response is electronic rather than direct response to the variable being measured. An example of an electronically calibrated instrument is a chart recorder. To perform the calibration, the "standard" consists of a constant or variable voltage output device. The instrument may or may not, include a mechanism for user adjustment. The instrument may allow the voltage to be checked at only one point (generally full-scale) or may permit mid-range checks. Most chart recorders also have a mechanism for adjustment of the zero offset. If the instrument permits multiple-point checks and user adjustment, then the calibration should consist of a check of zero voltage and 2 to 4 points corresponding to approximately equal divisions of the full-scale range, with the uppermost point being at 75 to 90 percent of full-scale. Such calibrations and adjustments should be performed only by personnel trained in electronic calibration procedures.

The third type of calibration, against known standards, is the most common type. In it, the instrument is exposed to standards of known concentration, generally traceable to national institute of Standards and Technology (NIST) standards. Standards obtainable from NIST are termed primary standards; while the concentration is known to a high certitude, the cost is also high. Secondary standards (often termed "NIST-traceable") are of much lower cost and are more readily obtainable. Secondary standards are usually adequate for most instrument calibrations. A calibration procedure of this type should include a zero concentration (if applicable) or a near (2x) detection limit concentration, and 2 to 4 additional upscale points. The lowest of these points should be at least 3 times the detection limit or below the lowest concentration expected in the material to be sampled. The uppermost point should be greater than the highest concentration expected in the sample material. Thus, the calibration should "bracket" the expected sample concentrations. All points should be run without any adjustment to the instrument. If one or more points fails to meet the established acceptance window, then adjustments are to be made and all points rerun. This procedure continues until no more adjustment is needed and all points are within acceptance criteria.

Calibration frequency varies among instrument types. Generally, factory calibration intervals are recommended by the manufacturer and electronic calibration intervals may also be recommended. For all types of calibration, it is recommended that calibration be checked on a regular basis (for example, prior to each use or once per week). Records of these calibration or quality control checks (QCC) should be maintained and, if feasible, graphed. These checks will show the drift in the calibration curve; based on this drift, the frequency of calibration can be

increased or decreased to correspond to the drift tendency. The QCC may be a one- to three-point check, using standards from a different source than those used for calibration.

Calibration types, standards used, and frequency are given in the indicator-specific sections. Calibrations procedures are provided in field operations manuals, standard methods, and standard operating procedures.

4.0 INFORMATION MANAGEMENT

Like quality assurance (QA), information management (IM) is integral to all aspects of EMAP surface water research projects, from initial selection of sampling sites through dissemination and reporting of final, validated data. Quality assurance and quality control (QC) measures implemented for the IM system are aimed at preventing corruption of data at the time of their initial incorporation into the system and maintaining the integrity of data and information after incorporation into the system. The general organization of, and QA/QC measures associated with, the IM system are described in this section.

4.1 Overview of System Structure

At each point where data and information are generated, compiled, or stored, the information must be managed. Thus, the IM system includes all of the data-generating activities, all of the means of recording and storing information, and all of the processes which use data. The IM system includes both hardcopy and electronic means of generating, storing, and archiving data. All participants in EMAP surface waters research projects have certain responsibilities and obligations which make them a part of the IM system. In its entirety, the IM system includes site selection and logistics information, sample labels and field data forms, tracking records, map and analytical data, data validation and analysis processes, reports, and archives. IM staff supporting EMAP surface waters research at WED provide support and guidance to all program operations in addition to maintaining a central data base management system for EMAP surface waters research data.

The central repository for data and associated information collected for use by EMAP - SW is a DEC Alpha server system located at WED-Corvallis. The general organization of the information management system is presented in Figure 6. Data are stored and managed on this system using the Statistical Analysis System (SAS) software package. This centrally managed im system is the primary data management center for EMAP surface waters research conducted at WED and elsewhere. The IM staff receives, enters, and maintains data and information generated by the site selection process (see Section 3 and Figure 3), field sample and data collection, map-based measurements, laboratory analyses, and verification and validation activities completed by the indicator leads. In addition to this inflow, the IM system provides

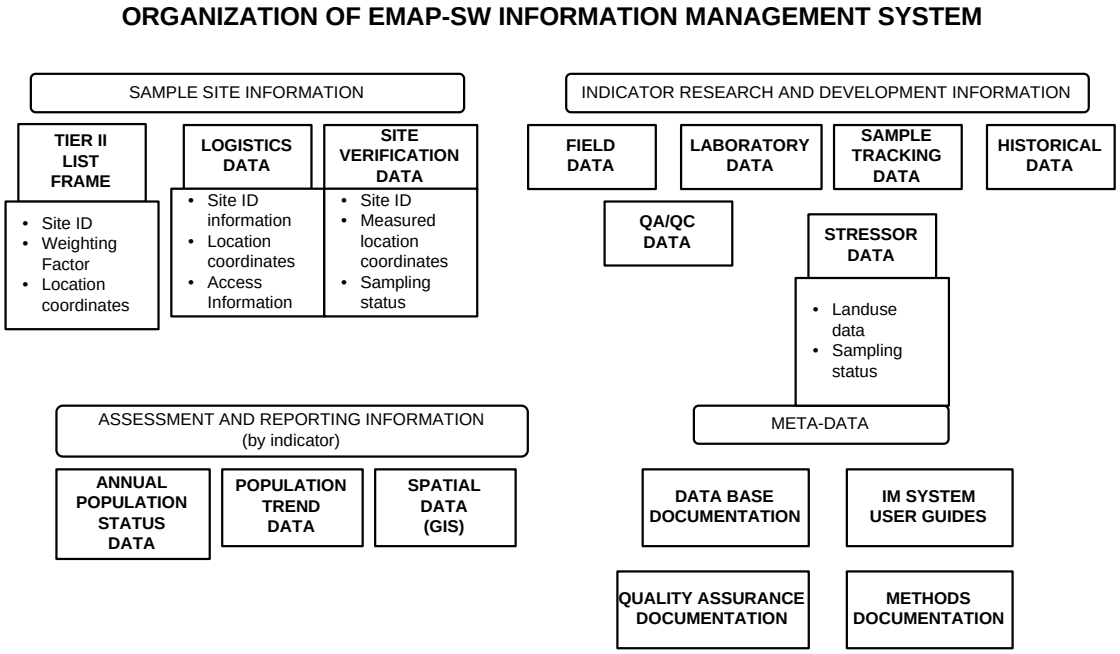

Figure 6. Organization of information management system for EMAP surface waters research activities.

outflow in provision of data files to EMAP surface water research staff, and other users. The IM staff at WED is responsible for maintaining the security integrity of both the data and the system.

The following sections describe the major inputs to the central data base and the associated QA/QC processes used to record, enter, and validate measurement and analytical data collected for EMAP surface waters research projects. Activities to maintain the integrity and assure the quality of the contents of the IM system are also described.

4.1.1 Design and Logistics Data Bases

The site selection process described in Section 3 produces a list of candidate sampling locations, inclusion probabilities, and associated site classification data (e.g., target status, ecoregion, size class, etc.). This "design" data base is provided to the IM staff, implementation coordinators, and field coordinators. Field coordinators determine ownership and contacts for acquiring permission to access each site, and conduct reconnaissance activities. Ownership and reconnaissance information for each site are compiled into a "logistics" data base. Generally, standardized forms are used during reconnaissance activities. Information from these forms may be entered into a SAS compatible data management system. Whether in electronic or hardcopy format, a copy of the logistics data base is provided to the IM for archival.

4.1.2 Sample Collection and Field Data Recording

Prior to initiation of field activities, the IM staff works with the indicator leads to develop standardized field data forms and sample labels. When possible, samples are labeled with a preprinted adhesive bar code label having a unique identification code. This identification code is linked to all required information for a particular sample that was recorded on the field data form. In cases where the use of bar code labels is impractical, preprinted adhesive labels having a standard recording format are completed and affixed to each sample container. Precautions are taken to ensure that label information remains legible and the label remains attached to the sample. Examples of sample labels are presented in the field operations manual.

Field sample collection and data forms are designed in conjunction with IM staff to ensure the format facilitates field recording and subsequent data entry tasks. All forms which may be used onsite are printed on water-resistant paper. Copies of the field data forms and

instructions for completing each form are documented in the field operations manuals. Recorded data are reviewed upon completion of data collection and recording activities by a person other than the one who completed the form. Field crews check completed data forms and sample labels before leaving a sampling site to ensure information and data were recorded legibly and completely. Errors are corrected if possible, and data considered as suspect are qualified using a flag variable. The field crew enters explanations for all flagged data in a comments section. Completed field data forms are transmitted to the IM staff at WED for entry into the central data base management system; indicator leads also receive copies of all field-recorded data.

If portable PCs are to be used in the field, user screens are developed which duplicate the standardized form to facilitate data entry. Specific output formats are available to print data for review and for production of shipping forms. Data may be transferred via modem on a daily basis. Each week floppy discs containing all down-loaded data for the week are mailed to the IMC. Detailed procedures for use of the PC, down-loading and transmittal of data, and printing of output files are presented in the field operations manuals.

All samples are tracked from the point of collection. If field PCs are used, tracking records are generated by custom-designed software. Hardcopy tracking and custody forms are completed if PCs are not available for use. Copies of the shipping and custody record accompany all sample transfers; other copies are transmitted to the IMC and applicable indicator lead. Samples are tracked to ensure that they are delivered to the appropriate laboratory, that lost shipments can be quickly identified and traced, and that any problems with samples observed when received at the laboratory are reported promptly so that corrective action can be taken if necessary.

Procedures for completion of sample labels and field data forms, and use of PCs are covered extensively in training sessions. General QC checks and procedures associated with sample collection and transfer, field measurements, and field data form completion for most indicators are listed in Table 7. Additional QA/QC checks or procedures specific to individual indicators are described in the indicator sections in Part II of this QAPP.

TABLE 7. SAMPLE AND FIELD DATA QUALITY CONTROL ACTIVITIES

Quality Control Activity	Description and/or Requirements
Contamination Prevention	All containers for individual site sealed in plastic bags until use; specific contamination avoidance measures covered in training
Sample Identification	Pre-printed labels with unique ID number on each sample
Data Recording	Data recorded on pre-printed forms of water-resistant paper; field crew reviews data forms for accuracy, completeness, and legibility
Data Qualifiers	Defined qualifier codes used on data form; qualifiers explained in comments section on data form
Sample Custody	Unique sample ID and tracking form information entered in LIMS; sample shipment and receipt confirmed
Sample Tracking	Sample condition inspected upon receipt and noted on tracking form with copies sent to Indicator Lead, Communications Center, and/or IM
Data Entry	Data entered using customized entry screens that resemble the data forms; entries reviewed manually or by automated comparison of double entry
Data Submission	Standard format defined for each measurement including units, significant figures, and decimal places, accepted code values, and required field width
Data Archival	All data archived in an organized manner for a period of seven years or until written authorization for disposition has been received from the Surface Waters Technical Director.

4.1.3 Laboratory Analyses and Data Recording

Upon receipt of a sample shipment, analytical laboratory receiving personnel check the condition and identification of each sample against the sample tracking record. Each sample is identified by information written on the sample label and by a barcode label. Any discrepancies, damaged samples, or missing samples are reported to the IM staff and indicator lead by telephone.

Most of the laboratory analyses for EMAP surface waters indicators, particularly chemical and physical analyses, follow or are based on standard methods. Standard methods generally include requirements for QC checks and procedures. General laboratory QA/QC procedures applicable to most EMAP surface water indicators are described in Table 8. Additional QA/QC samples and procedures specific to individual indicator analyses are

TABLE 8. LABORATORY DATA QUALITY CONTROL ACTIVITIES

Quality Control Activity	Description and/or Requirements
Instrument Maintenance	Follow manufacturer's recommendations and specific guidelines in methods; maintain logbook of maintenance/repair activities
Calibration	Calibrate according to manufacturer's recommendations and guidelines given in Section 6; recalibrate or replace before analyzing any samples
QC Data	Maintain control charts, determine MDLs and achieved data attributes; include QC data summary in submission package
Data Recording	Use software compatible with EMAP-SW IM system; check all data entered against the original bench sheet to identify and correct entry errors. Review other QA data (e.g. condition upon receipt, etc.) for possible problems with sample or specimens.
Data Qualifiers	Use defined qualifier codes; explain all qualifiers
Data Entry	Automated comparison of double entry or 100% manual check against original data form
Submission Package	Includes: Letter by the laboratory manager; data, data qualifiers and explanations; electronic format compatible with EMAP-SW IM system, documentation of file and data base structures, variable descriptions and formats; summary report of any problems and corrective actions implemented
Data Archival	All data archived in an organized manner for a period of seven years or until written authorization for disposition has been received from the Surface Waters Technical Director

described in the indicator sections in Part II of this QAPP. Biological sample analyses are generally based on current acceptable practices within the particular biological discipline. Some QC checks and procedures applicable to most EMAP surface waters biological samples are described in Table 9. Additional QA/QC procedures specific to individual biological indicators are described in the indicator sections in Part II of this QAPP.

TABLE 9. BIOLOGICAL SAMPLE QUALITY CONTROL ACTIVITIES

Quality Control Activity	Description and/or Requirements
Taxonomic Nomenclature	Use accepted common and scientific nomenclature and unique entry codes
Taxonomic Identifications	Use standard taxonomic references and keys; maintain bibliography of all references used
Independent Identifications	Uncertain identifications to be confirmed by expert in particular taxa
Duplicate Identifications	At least 5% of all samples completed per taxonomist reidentified by different analyst; less than 10% assigned different ID
Taxonomic Reasonableness Checks	Species or genera known to occur in given conditions or geographic area
Reference Collections	Permanent mounts or voucher specimens of all taxa encountered

A laboratory's IM system may consist of only hardcopy records such as bench sheets and logbooks, an electronic laboratory information management system (LIMS), or some combination of hardcopy and electronic records. Laboratory data records are reviewed at the end of each analysis day by the designated laboratory onsite QA coordinator or by supervisory personnel. Errors are corrected if possible, and data considered as suspect by laboratory analysts are qualified with a flag variable. All flagged data are explained in a comments section. Private contract laboratories generally have a laboratory quality assurance plan and established procedures for recording, reviewing, and validating analysis data.

Once analytical data have passed all of the laboratory's internal review procedures, a submission package is prepared and transferred to the IM staff and/or indicator lead. The contents of the submission package are largely dictated by the type of analysis (physical, chemical, or biological), but generally includes at least the elements listed in Tables 8 or 9. Remaining sample material and voucher specimens may be transferred to the indicator lead or archived by the laboratory, depending upon the arrangements desired by the indicator lead. All samples and raw data files (including logbooks, bench sheets, and instrument tracings) are to be retained for a period of seven years or until authorized for disposal, in writing, by the EMAP Director.

4.1.4 Data Review, Verification, Validation Activities

Raw data files are created from entry of field and analytical data, including data for QA/QC samples and any data qualifiers noted on the field forms or analytical data package. After initial entry, data are reviewed for entry errors by either a manual comparison of a printout of the entered data against the original data form or by automated comparison of data entered twice into separate files. Entry errors are corrected and reentered. For biological samples, species identifications are corrected for entry errors associated with incorrect or misspelled codes. Errors associated with misidentification of specimens are corrected after voucher specimens have been confirmed and the results are available. Files corrected for entry errors are considered to be raw data files. Copies of all raw data files are maintained in the centralized IM system.

The indicator lead is ultimately responsible for validation and verification of all data. A copy of the raw data files are maintained in the central IM system, generally in active files until completion of reporting and then in archive files. Redundant copies are maintained of all data files and all files are periodically backed up.

Some of the typical checks made in the processes of verification and validation are described in Table 10. Additional checks specific to individual indicators are described in the indicator sections in Part II of this QAPP. Automated review procedures may be used. The primary purpose of the initial checks is to confirm that a data value present in an electronic data file is accurate with respect to the value that was initially recorded on a data form or obtained from an analytical instrument. In general, these activities focus on individual variables in the raw data file and may include range checks for numeric variables, frequency tabulations of coded or alphanumeric variables to identify erroneous codes or misspelled entries, and summations of variables reported in terms of percent or percentiles. In addition, associated QA information (e.g., sample holding time) and QC sample data are reviewed to determine if they meet acceptance criteria. Suspect values are assigned a data qualifier until they can be corrected or confirmed as unacceptable and replaced with a new acceptable value from sample reanalysis.

A second review is conducted after all analyses have been completed and the raw data file is created. The internal consistency among different analyses or measurements conducted on a sample is evaluated. Examples of internal consistency checks include calculation of chemical ion balances or the summation of the relative abundances of taxa. Samples identified as suspect

TABLE 10. DATA REVIEW, VERIFICATION, AND VALIDATION QUALITY CONTROL ACTIVITIES

Quality Control Activity	Description and/or Requirements
Review any qualifiers associated with variable	Determine if value is suspect or invalid; assign validation qualifiers as appropriate
Summarize and review replicate sample data	Identify replicate samples with large variance; determine if analytical error or visit-specific phenomenon is responsible
Determine if data quality objectives have been achieved	Determine potential impact on achieving research and/or program objectives
Exploratory data analyses (univariate, bivariate, multivariate) utilizing all data	Identify outlier values and determine if analytical error or site-specific phenomenon is responsible
Confirm assumptions regarding specific types of statistical techniques being utilized in development of metrics and indicators	Determine potential impact on achieving research and/or program objectives

based on internal consistency checks are qualified with a flag variable and targeted for more intensive review. Data remain qualified until they can be corrected, are confirmed as acceptable in spite of the apparent inconsistency, or until new acceptable values are obtained from sample reanalysis. Upon completion of these activities, copies of the resultant data files are transmitted for archival storage.

In the final stage of data verification and validation, exploratory data analysis techniques may be used to identify extreme data points or statistical outliers in the data set. Examples of univariate analysis techniques include the generation and examination of box-and-whisker plots and subsequent statistical tests of any outlying data points. Bivariate techniques include calculation of Spearman correlation coefficients for all pairs of variables in the data set with subsequent examination of bivariate plots of variables having high correlation coefficients. Recently, multivariate techniques have been used in detecting extreme or outlying values in environmental data sets (Meglen, 1985; Garner et al., 1991; Stapanian et al., 1993). A software package, SCOUT, developed by EPA and based on the approach of Garner et al. (1991) may be used for validation of multivariate data sets.

Suspect data are reviewed to determine the source of error, if possible. If the error is correctable, the data set is edited to incorporate the correct data. If the source of the error cannot be determined, data are qualified as questionable or invalid. Data qualified as questionable may

be acceptable for certain types of data analyses and interpretation activities. The decision to use questionable data must be made by the individual data users. Data qualified as invalid are considered to be unacceptable for use in any analysis or interpretation activities and will generally be removed from the data file and replaced with a missing value code and explanatory comment or flag code. After completion of verification and validation activities, a final data file is created, with copies transmitted for archival and for uploading to the centralized IM system.

Once verified and validated, data files are made available for use in various types of interpretation activities, each of which may require additional restructuring of the data files. These restructuring activities are collectively referred to as "data enhancement." In order to develop indicator metrics from one or more variables, data files may be restructured so as to provide a single record per lake. To calculate lake population estimates based on individual measurements or indicators, missing values, and suspect data points may need to be replaced with alternate data (such as a value from a replicate measurement) or values calculated from predictive relationships based on other variables.

4.2 Data Transfer

Field crews may transmit data electronically via modem or floppy disc; hardcopies of completed data and sample tracking forms may be transmitted to the IM staff at WED via portable facsimile (FAX) machine or via express courier service. Copies of raw, verified, and validated data files are transferred from indicator leads to the IM staff for inclusion in the central IM system. All transfers of data are conducted using a means of transfer, file structure, and file format that has been approved by the IM staff. Data files that do not meet the required specifications will not be incorporated into the centralized data access and management system.

4.3 Hardware and Software Control

All automated data processing (ADP) equipment and software purchased for or used in EMAP surface waters research is subject to the requirements of the federal government, the particular Agency, and the individual facility making the purchase or maintaining the equipment and software. All hardware purchased by EPA is identified with an EPA barcode tag label; an

inventory is maintained by the responsible ADP personnel at the facility. Inventories are also maintained of all software licenses; periodic checks are made of all software assigned to a particular PC.

All software developed specifically for EMAP surface waters research activities is tested and documented. Test data sets are designed to fully test the capabilities and equations in the program. Documentation includes internal software documentation, data dictionaries, and user's guide information. Most of the documentation is available on-line, to facilitate user access to the needed information. In addition to data base documentation, all programs developed for use in the IM system is documented and tested. Source code programs include internal documentation to facilitate debugging and subsequent revision. User guides for all software developed or used for IM activities are prepared or purchased commercially.

The development and organization of the IM system is compliant with guidelines and standards established by the EMAP Information Management Technical Coordination Group, the EPA office of information resources management (OIRM), and the EPA office of Administrative Resources Management (OARM). Areas addressed by these policies and guidelines include, but are not limited to, the following:

- Taxonomic Nomenclature and Coding
- Locational data
- Sampling unit identification and reference
- Hardware and software
- Data catalog documentation

EMAP is committed to compliance with all applicable regulations and guidance concerning hardware and software procurement, maintenance, configuration control, and QA/QC. As new guidance and requirements are issued, the EMAP surface waters information management staff will assess the impact upon the IM system and develop plans for ensuring timely compliance.

4.4 Data Security

All data files in the IM system are protected from corruption by computer viruses, unauthorized access, and hardware and software failures. Guidance and policy documents of

EPA and management policies established by the EMAP IM Technical Coordination Group for data access and data confidentiality are followed. Raw and verified data files are accessible only to EMAP surface water research partners. Validated data files are accessible only to users specifically authorized by the EMAP Director. Data files in the central repository used for access and dissemination are marked as read-only to prevent corruption by inadvertent editing, additions, or deletions.

Data generated, processed, and incorporated into the IM system are routinely stored as well as archived on redundant systems. This ensures that if one system is destroyed or incapacitated, IM staff will be able to reconstruct the data bases. Procedures developed to archive the data, monitor the process, and recover the data are described in IM documentation.

Several backup copies of all data files and of the programs used for processing the data are maintained. Backups of the entire system are maintained off-site. System backup procedures are utilized. The central data base is backed up and archived according to procedures already established for WED. All laboratories generating data and developing data files must have established procedures for backing up and archiving computerized data.

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PART II

INDICATORS

Part II is comprised of separate sections detailing the quality assurance information for individual indicators. These indicator-specific sections describe how the policies and procedures presented in Part I are implemented for each indicator. Thus, Part II should be considered a supplement to Part I.

Each indicator section is similarly formatted. An introductory section describes the indicator, long-term objectives, and relationship to historical monitoring programs, if applicable. The questions to be addressed or hypotheses to be tested in this year's monitoring are provided, if available. Also, if available, the data analysis plan is briefly described. The sampling design section describes the index sample collection design; the overall sampling design (i.e., which indicators are sampled at which site types) is described in Section 3.2 of Part I. The sampling and analytical methods section provides a brief description and/or reference for the sampling and analytical methodologies; the user is referred to the field and laboratory manuals and/or cited references for detailed sampling and analytical procedure descriptions. The data quality objectives section provides the measurement quality objectives or data quality objectives in terms of precision, accuracy or bias, completeness, comparability, representativeness, and method detection limit, as applicable to the indicator measurements. The next two sections describe the quality control procedures for the field and laboratory, respectively. These sections describe the QA/QC samples and QC procedures used to ensure the collection of high quality samples and data. Section 2 of Part I provides definitions of these data quality attributes, descriptions of the types and uses of QA/QC samples, and equations. The individual indicator data management system, data review procedures, and verification/validation criteria are described in the final section. The central EMAP-SW data management system is described in Section 4 of Part I. Each section also contains a references list.

The format used is designed to facilitate documentation of indicator development. These sections are reviewed and updated by the Indicator Leads on an annual basis. Additionally, this format is designed to facilitate distribution, in that only the applicable indicator sections need be included in the distribution to specific groups (for example, streams field teams need only receive the sections for indicators sampled in streams). Finally, this format is designed to facilitate the addition of new indicators and deletion of others as the EMAP-SW program moves towards full implementation. For these reasons, the individual sections are numbered internally, but are not assigned an overall section number. Instead, the header block on each page identifies the indicator by name, thus permitting rapid location of the sections of interest to the user.

Each indicator is being developed at its own pace. Section 3 of Part I contains a table which lists the current status of the indicator (candidate or core) and the QA category as described in Simes (1991). In general, the

QA category relates to the degree of development of the individual indicator QA program. Thus, a section for a Category II indicator can be expected to be more detailed than a section for a Category III indicator. As indicators move from candidate to core status, it is expected that the QA category will change from IV or III to II or I and that this will be reflected in the detail and completeness of the indicator section.

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Simes, G.F. 1991. *Preparation Aids for the Development of Category I(II, III, and IV) Quality Assurance Project Plans*. EPA600/8-91/003(004, 005, and 006). U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C.

WATER CHEMISTRY INDICATOR (STREAMS)

1.0 INTRODUCTION

Ecological indicators based on lake and stream water chemistry information attempt to evaluate stream condition with respect to stressors such as acidic deposition and other types of physical or chemical contamination. Data are collected for a variety of physical and chemical constituents to provide information on the acid-base status of each lake and stream (of importance to the TIME project), water clarity, primary productivity, nutrient status, mass balance budgets of constituents, color, temperature regime, and presence and extent of anaerobic conditions.

There are two components to collecting water chemistry information: collecting samples of stream water to ship to the analytical laboratory, and field or in situ measurements of specific conductance, dissolved oxygen, and water temperature. At each site, crews fill one 4-L Cubitainer and two or more 60-mL syringes with stream water. These samples are stored in a cooler packed with Ziploc tabs filled with ice and shipped to the analytical laboratory within 24 hours of collection. In situ measurements are made using field meters and recorded on standardized data forms. The primary function of the water chemistry information is to determine:

- Acid-base status
- Trophic state (nutrient enrichment)
- Chemical stressors
- Classification of water chemistry type

Specific research questions and hypotheses to be addressed from this year's activities are listed in Table 1-1.

2.0 SAMPLING DESIGN

The plot design for stream sampling is shown in Figure 2-1. The plot design for water chemistry sampling is based on that used for the National Stream Survey (Kaufmann et al. 1988). At each stream, a single index site located at the midpoint of the designated stream reach. At each index site, a single water sample is collected, and a single set of in situ or field measurements are conducted to provide a representation of the stream's condition with respect to its chemical constituents. Revisits conducted at a subset of stream sites within the index sampling period provide data to estimate temporal variability over the index period. Return visits to streams sampled in previous years provide data to estimate annual variability (see Part I, Section 3).

Table 1-1. Research Questions and Hypotheses: Water Chemistry Indicator

EMAP Design Evaluation: Obtain estimates of annual regional variation and index period variation.
Indicator Development and Evaluation: Development of chemical classes based on different types of chemical stressors (e.g., acid min drainage), examine relationship of chemical condition/stress to watershed landuse, and develop indicator(s) of of chemical condition (e.g., trophic state [Carlson, 1968]).
Other (TIME): Annual collection of probability data on regional acid-base status for trend monitoring.

3.0 SAMPLING AND ANALYTICAL METHODOLOGIES

Sample Collection: At the stream index site, a water sample is prepared from a series of 500-mL grab samples collected from the upper portion of the water column (Figure 2-1). These grab samples are composited into a single 4-L bulk water sample. Two to four syringe samples for closed system measurements are collected by immersing each syringe into the stream at the index site and drawing water from under the surface into the syringe without exposure to the atmosphere. Detailed procedures for sample collection are described in the field operations manual.

Field Measurements: Detailed procedures for conducting field measurements for streams are described in the field operations manual. Field measurements for streams are conducted in situ or at streamside on a grab sample of water. Table 3-1 summarizes methods for field and in situ water column measurements for lakes and streams. These methods are based on standard limnological methods or validated EPA methods.

Analysis: Laboratory analyses are identical for both lake and stream samples. Table 3-2 summarizes analytical methodologies. Analytical methods are based on EPA validated methods, modified for use with aqueous samples of low ionic strength. Modified methods are thoroughly documented in the laboratory methods handbook prepared for the Aquatic Effects Research Program (AERP; U.S. EPA, 1987).

Table 3-1. Field Measurement Methods: Water Chemistry Indicator

Variable or Measurement	QA Class[a]	Expected Range	Summary of Method	References
Temperature, in situ	C	4 to 30 EC	Measured at mid-channel using thermistor probe.	EPA 150.6; Chaloud et al. (1989)
Dissolved oxygen, in situ	C	0 to 14 mg O_2/L	Measured at mid-channel (streams) using membrane electrode and meter.	EPA 360.1; Chaloud et al. (1989)
Conductivity, field	N	10 to 1000 µS/cm @ 25 °C	Conductivity meter; reading corrected to 25 °C	EPA 360.1

[a] C = critical, N = non-critical quality assurance classification.

INDEX SAMPLE COLLECTION: WATER CHEMISTRY INDICATOR

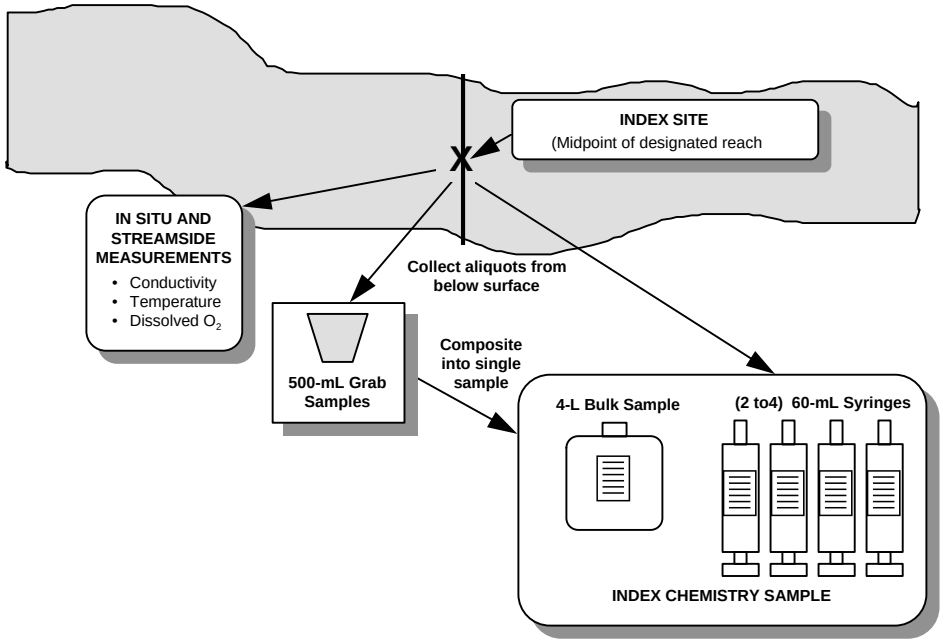

Figure 2-1. Lake and stream index sampling design for the water chemistry indicator.

Table 3-2. Analytical Methodologies: Water Chemistry Indicator

Analyte	QA Class	Expected Range	Summary of Method	References
pH, closed system	C	3 to 9 pH units	Sample collected and analyzed without exposure to atmosphere; electrometric determination (pH meter and glass combination electrode)	EPA 150.6 (modified); U.S. EPA (1987)
pH, equilibrated	N	3 to 9 pH units	Equilibration with 300 ppm CO_2 for 1 hr prior to analysis; Electrometric determination (pH meter and glass combination electrode)	EPA 150.6 (modified); U.S. EPA (1987)
Acid Neutralizing Capacity (ANC)	C	-100 to 5,000 µeq/L	Acidimetric titration to pH # 3.5, with modified Gran plot analysis	EPA 310.1 (modified); U.S. EPA (1987)
Carbon, dissolved[a] inorganic (DIC), closed system	N	0.1 to 50 mg C/L	Sample collected and analyzed without exposure to atmosphere; acid-promoted oxidation to CO_2, with detection by infrared spectrophotometry	U.S. EPA (1987)
Carbon, dissolved organic (DOC)	C	0.1 to 30 mg C/L	UV-promoted persulfate oxidation, detection by infrared spectrophotometry.	EPA 415.2, U.S. EPA (1987)
Conductivity	C	1 to 500 µS/cm	Electrolytic (conductance cell and meter)	EPA 120.6, U.S. EPA (1987)
Aluminum, total dissolved	C	10 to 1,000 µg/L	Atomic absorption spectroscopy (graphite furnace)	EPA 202.2; U.S. EPA (1987)
Aluminum, monomeric and organic monomeric	N	0 to 500 µg/L	Collection and analysis without exposure to atmosphere. Portion of sample passed through a cation exchange column before analysis to obtain estimate of organic-bound fraction. Colorimetric analysis (automated pyrocatechol violet).	APHA 3000-Al E.; APHA (1989), U.S. EPA (1987)

(continued)

C = critical, N = non-critical quality assurance classification.
[a] For DIC, "dissolved" is defined as that portion passing through a 0.45 µm nominal pore size filter. For other analytes, "dissolved" is defined as that portion passing through a 0.4 µm pore size filter (Nucleopore or equivalent).

Table 3-2 (continued)

Analyte	QA Class	Expected Range	Summary of Method	References
Major Cations (dissolved)				
Calcium	C	0.02 to 76 mg/L (1 to 3,800 µeq/L)	Atomic absorption spectroscopy (flame)	EPA 200.6, U.S. EPA (1987)
Magnesium	C	0.01 to 25 mg/L (1 to 2,000 µeq/L)		
Sodium	C	0.01 to 75 mg/L (0.4 to 3.3 µeq/L)		
Potassium	C	0.01 to 10 mg/L (0.3 to 250 µeq/L)		
Ammonium	N	0.01 to 5 mg/L (0.5 to 300 µeq/L)	Colorimetric (automated phenate)	EPA 350.7; U.S. EPA (1987)
Major Anions, dissolved				
Chloride	C	0.03 to 100 mg/L (1 to 2,800 µeq/L)	Ion chromatography	EPA 300.6; U.S. EPA (1987)
Nitrate	C	0.06 to 20 mg/L (0.5 to 350 µeq/L)		
Sulfate	C	0.05 to 25 mg/L (1 to 500 µeq/L)		
Silica, dissolved	N	0.05 to 15 mg/L	Automated colorimetric (molybdate blue)	EPA 370.1 (modified), U.S. EPA (1987)
Phosphorus, total	C	0 to 1000 µg/L	Acid-persulfate digestion with automated colorimetric determination (molybdate blue)	USGS I-4600-78; Skougstad et al. (1979), U.S. EPA (1987)

(continued)

C = critical, N = non-critical quality assurance classification.

[a] For DIC, "dissolved" is defined as that portion passing through a 0.45 µm nominal pore size filter. For other analytes, "dissolved" is defined as that portion passing through a 0.4 µm pore size filter (Nucleopore or equivalent).

Table 3-2 (continued)

Analyte	QA Class	Expected Range	Summary of Method	References
Nitrogen, total	N	0 to 25,000 µg/L	Alkaline persulfate digestion with determination of nitrate by cadmium reduction and determination of nitrite by automated colorimetry (EDTA/sulfanilimide).	EPA 353.2 (modified); U.S. EPA (1987)
True Color	N	0 to 300 Platinum Cobalt Units (PCU)	Visual comparison to calibrated glass color disks	EPA 100.2 (modified), APHA 204 A.; U.S. EPA (1987)
Turbidity	N	1 to 100 Nephelometric Turbidity Units (NTU)	Nephelometric	APHA 214 A., EPA 180.1; U.S. EPA (1987)
Total Suspended Solids (TSS)	N	1 to 200 mg/L	Gravimetric	EPA 160.3; APHA (1989)

C = critical, N = non-critical quality assurance classification.
[a] For DIC, "dissolved" is defined as that portion passing through a 0.45 µm nominal pore size filter. For other analytes, "dissolved" is defined as that portion passing through a 0.4 µm pore size filter (Nucleopore or equivalent).

4.0 QUALITY ASSURANCE OBJECTIVES

Measurement data quality objectives (measurement DQOs or MQOs) are given in Table 4-1. General requirements for comparability and representativeness addressed in Part I, Section 4. The MQOs given in Table 4-1 represent the maximum allowable criteria for statistical control purposes. Method detection limits are monitored over time by repeated measurements of low level standards and calculated using Equation 4-1. For major cations and anions, the required MDLs are approximately equivalent to 1.0 µeq/L (0.5 µeq/L for nitrate). Analytical laboratories may report results in mg/L; these results are converted to µeq/L for interpretation. For total suspended solids determinations, the "detection limit" is defined based on the required sensitivity of the analytical balance.

Table 4-1. Measurement Data Quality Objectives: Water Chemistry Indicator

Variable or Measurement	Method Detection Limit	Precision and Accuracy	Transition Value[a]	Completeness
Oxygen, dissolved	NA	±0.5 mg/L	NA	95%
Temperature	NA	±1 ±C	NA	95%
pH, closed system and equilibrated	NA	±0.075 or ±0.15 pH units	pH 5.75	95%
Acid Neutralizing Capacity	NA	±5 µeq/L or ±5%	100 µeq/L	95%
Carbon, dissolved inorganic, closed system	0.10 mg/L	0.10 mg/L or 10%	1 mg/L	95%
Carbon, dissolved organic	0.1 mg/L	±0.1 mg/L or ±10%	1 mg/L	95%
Conductivity	NA	±1 µS/cm or ±2%	50 µS/cm	95%
Aluminum, total dissolved, total monomeric, and organic monomeric	10 µg/L	±10 µg/L or ±10%	100 µg/L	95%
Major Cations:				95%
Calcium	0.02 mg/L	±0.02 mg/L or ±5%	0.4 mg/L	
Magnesium	0.01 mg/L	±0.01 mg/L or ±5%	0.2 mg/L	
Sodium	0.02 mg/L	±0.02 mg/L or ±5%	0.4 mg/L	
Potassium	0.04 mg/L	±0.04 mg/L or ±5%	0.8 mg/L	
Ammonium	0.02 mg/L	±0.02 mg/L or ±5%	0.4 mg/L	95%
Major Anions:				95%
Chloride	0.03 mg/L	±0.03 mg/L or ±5%	0.6 mg/L	
Nitrate	0.03 mg/L	±0.03 mg/L or ±5%	0.6 mg/L	
Sulfate	0.05 mg/L	±0.05 mg/L or ±5%	1 mg/L	
Silica	0.05 mg/L	±0.05 mg/L or ±5%	1 mg/L	95%
Phosphorus, total	1 µg/L	±1 µg/L or ±5%	20 µg/L	95%
Nitrogen, total	1 µg/L	±1 µg/L or ±5%	20 µg/L	95%
True Color	NA	±5 PCU or ±10%	50 PCU	95%
Turbidity	NA	±2 NTU or ±10%	20 NTU	95%
Total Suspended Solids	0.1 mg	±1 mg/L or ±10%	10 mg/L	95%

NA = not applicable
[a] Represents the value above which precision and bias are expressed in relative terms.

For precision, the objectives presented in Table 4-1 represent the 99 percent confidence intervals about a single measurement and are thus based on the standard deviation of a set of repeated measurements ($n > 1$). Precision objectives at lower concentrations are equivalent to the corresponding MDL. At higher concentrations,

the precision objective is expressed in relative terms, with the 99 percent confidence interval based on the relative standard deviation (Part I, Section2). Objectives for accuracy are equal to the corresponding precision objective, and are based on the mean value of repeated measurements. Accuracy is generally estimated as net bias or relative net bias (Part I, Section 2). For total phosphorus and total nitrogen measurements, accuracy is also determined from analyses of matrix spike samples (also sometimes called fortified samples) as percent recovery (Part I, Section 2). Precision and bias are monitored at the point of measurement (field or analytical laboratory) by several types of QC samples described in the Section 6.0, and from performance evaluation (PE) samples

The completeness objectives are established for each measurement *per site type* (e.g., EMAP probability sites, revisit sites). Failure to achieve the minimum requirements for a particular site type results in regional population estimates having wider confidence intervals. Failure to achieve requirements for repeat and annual revisit samples reduces the precision of estimates of index period and annual variance components, and may impact the representativeness of these estimates because of possible bias in the set of measurements obtained.

5.0 QUALITY CONTROL PROCEDURES: FIELD OPERATIONS

The general quality control process for stream field measurements is illustrated in Figure 5-1. Additional information for specific QC measurements are summarized in Table 5-1. Guidelines and requirements for recording field measurements and observations are presented in Section 7.0 (see also Part I, Section 4). Procedures for calibration of field instruments, conducting QC activities, and recording data for each measurement are described in the field operations manuals for lakes and streams.

Quality control activities and requirements pertaining to the collection and transport of samples to the laboratory are presented in Table 5-2. Collection and handling procedures for water samples to ensure compliance with these requirements are documented in the lake and stream field operations manuals. Guidelines and requirements associated with sample labeling and tracking are presented in Section 6.0.

6.0 QUALITY CONTROL PROCEDURES: LABORATORY OPERATIONS

6.1 Sample Receipt and Processing

Quality control activities associated with sample receipt and processing are presented in Table 6-1. The communications center and information management staff are notified of sample receipt and any associated problems as soon as possible after samples are received. The general schemes for processing stream water chemistry samples for analysis is presented in Figure 6-1. In addition to the four syringes prepared in the field, several additional aliquots are prepared from bulk water samples. Ideally, all analyses are completed within a few days after processing to allow for review of the results and possible

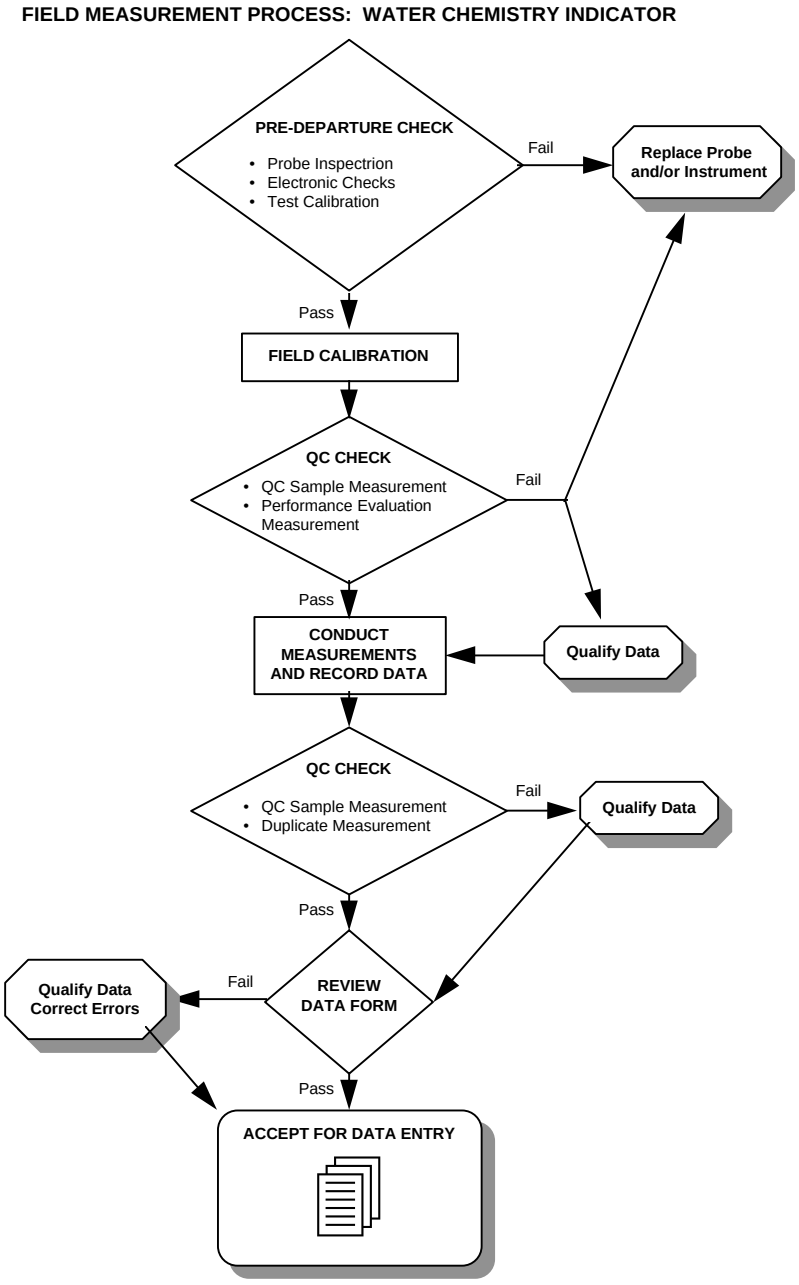

Figure 5-1. Field measurements activities for the water chemistry indicator.

Table 5-1. Field Quality Control Samples: Water Chemistry Indicator

Measurement	QC Sample Type	Description	Frequency	Acceptance Criteria	Corrective Action
Dissolved Oxygen	PE Sample	Concurrent determination of sample by Winkler titration	Once per meter	Measured O_2 within ±1 mg/L of O_2 estimated by Winkler titration	Replace meter and/or probe
	QC Check Sample	Water-saturated air	Daily (at base station)	Instrument can be calibrated to theoretical value	Replace meter and/or probe
Temperature	PE Sample	Concurrent measurement of 0 °C and 25 °C solutions with NIST-traceable thermometer	Once per meter	Within ±1 °C of thermometer reading	Replace probe and/or meter
	QC Check Sample	Concurrent measurement of sample with field thermometer	Weekly	Within ±1 °C of thermometer reading	Replace probe and/or meter
Conductivity	QC Check Sample	Solution of known conductivity	Weekly	Within 10 µS/cm of theoretical value	Re-calibrate meter using NIST-traceable standards; replace probe and/or meter

Table 5-2. Field Quality Control: Water Chemistry Indicator

QC Activities	Requirements
Sample Container Preparation and Handling	Rinse bulk containers and soak for 48 h with ASTM Type II reagent water; test water for conductivity; seal in plastic bags for shipment
Sample volumes	Minimum volume of bulk sample= 3 L Minimum volume of syringe sample= 50 mL
Storage Conditions (from collection until receipt at laboratory)	Maintain bulk and syringe samples in darkness at stream temperature, chill to approximately 4 EC as soon as possible after collection.
Shipping requirements	Ship directly to laboratory by the day after collection. Ship via overnight air courier in UN-approved containers that maintain required storage conditions.

Table 6-1. Sample Processing Quality Control: Water Chemistry Indicator

Quality Control Activity	Description and Requirements	Corrective Action
Sample Storage	Store samples in darkness at 4 °C Monitor temperature daily	Qualify sample as suspect for all analyses
Holding time	Complete processing bulk samples within 48 hours of collection	Qualify samples
Aliquot Containers and Preparation	Amber HDPE bottles required. Rinse bottles and soak for 48 h with ASTM Type II reagent water; test water for conductivity; seal in plastic bags for shipment Prepare bottles to receive acid as preservative by filling with a 10% HCl solution and allow to stand overnight. Rinse six times by filling with deionized water. Determine the conductivity of the final rinse of every tenth bottle. Conductivity must be < 2 µS/cm.	Repeat the deionized water rinsing procedure on all bottles cleaned since the last acceptable check. Check conductivity of final rinse on every fifth bottle.
Filtration	0.4 µm polycarbonate filters required for all dissolved analytes except DIC (0.45 µm) Rinse filters and filter chamber twice with 50-ml portions of deionized water, followed by a 20-mL portion of sample. Repeat for each filter used on a single sample. Rinse aliquot bottles with two 25 to 50 mL portions of filtered sample before use.	
Preservation	Use ultrapure acids for preservation. Add sufficient acid to adjust to pH < 2. Check pH with indicator paper. Record volume of preservative on container label. Store preserved aliquots in darkness at 4 °C until analysis.	
Holding Times for preserved aliquots	Closed system determinations from syringe samples must be completed within 72 hours of collection. Holding times for other analyses holding times range from 3 days to 6 months, based upon current APHA criteria.	Sample results are qualified as being in violation of holding time requirements.

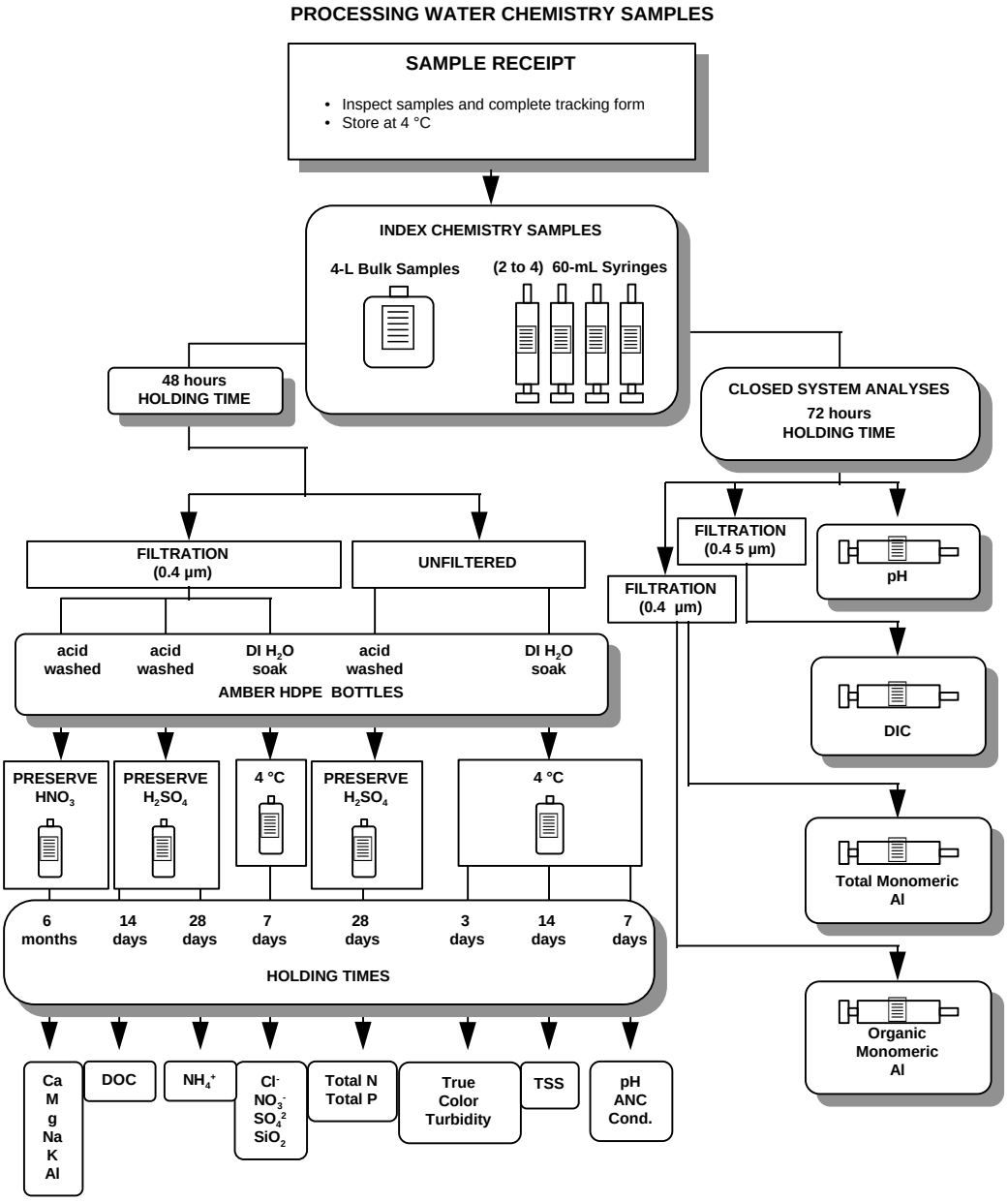

Figure 6-1. Sample processing activities for water chemistry samples.

reanalysis of suspect samples within seven days. Critical holding times for the various analyses are the maximum allowable holding times, based on current EPA and American Public Health Association (APHA) requirements (American Public Health Association, 1989). Analyses of samples after the critical holding time is exceeded will likely not provide representative data.

6.2 Analysis of Samples

Quality control protocols are an integral part of all analytical procedures to ensure that the results are reliable and the analytical stage of the measurement system is maintained in a state of statistical control. Most of the quality control procedures described here are detailed in the references for specific methods. However, modifications to the procedures and acceptance criteria described in this QAPP supersede those presented in the methods references. Information regarding QC sample requirements and corrective actions are summarized in Table 6-2. Figure 6-2 illustrates the general scheme for analysis of a batch of water chemistry samples, including associated QC samples.

Table 6-2. Laboratory Quality Control Samples: Water Chemistry Indicator

QC Sample Type (Analytes), and Description	Frequency	Acceptance Criteria	Corrective Action
Laboratory Blank: (all analyses except pH and total suspended solids[TSS]) Reagent Blank: (DOC, Al [total, monomeric, and organic monomeric], ANC, NH_4^+, SiO_2)	Once per batch prior to sample analysis.	Control limits < ±MDL	Prepare and analyze new blank. Determine and correct problem (e.g., reagent contamination, instrument calibration, or contamination introduced during filtration) before proceeding with any sample analyses.Reestablish statistical control by analyzing three blank samples.
Filtration Blank: (All dissolved analytes, excluding syringe samples) ASTM Type II reagent water processed through filtration unit.	Prepare once per week and. archive.	Measured concentrations < MDL	Measure archived samples if review of other laboratory blank information suggest source of contamination is sample processing
Detection Limit Quality Control Check Sample (QCCS): (All analyses except true color, turbidity, and TSS) Prepared so concentration is approximately four to six times the required MDL.	Once per batch	Control limits < ±MDL	Confirm achieved MDL by repeated analysis of appropriate standard solution. Evaluate affected samples for possible re-analysis.

(continued)

Table 6-2. (continued)

QC Sample Type (Analytes), and Description	Frequency	Acceptance Criteria	Corrective Action
Calibration QCCS: For turbidity, a QCCS is prepared at one level for routine analyses (U.S. EPA, 1987). Additional QCCSs are prepared as needed for samples having estimated turbidities greater than 20 NTU. For total suspended solids determinations, QCCS is a standard weight having mass representative of samples.	Before and after sample analyses	Control limits < precision objective: Mean value < bias objective	Repeat QCCS analysis. Recalibrate and analyze QCCS. Reanalyze all routine samples (including PE and field replicate samples) analyzed since the last acceptable QCCS measurement.
Internal Reference Sample: (Suggested when available for a particular analyte)	One analysis in a minimum of five separate batches	Control limits < precision objective. Mean value < bias objective	Analyze standard in next batch to confirm suspected imprecision or bias. Evaluate calibration and QCCS solutions and standards for contamination and preparation error. Correct before any further analyses of routine samples are conducted. Reestablish control by three successive reference standard measurements which are acceptable. Qualify all sample batches analyzed since the last acceptable reference standard measurement for possible reanalysis.

(continued)

Table 6-2. (continued)

QC Sample Type (Analytes), and Description	Frequency	Acceptance Criteria	Corrective Action
Laboratory Replicate Sample: (All analyses) For closed system analyses, a replicate sample represents a second injection of sample from the sealed syringe.	One per batch	Control limits < precision objective	If results are below MDL Prepare and analyze split from different sample (volume permitting). Review precision of QCCS measurements for batch. Check preparation of split sample. Qualify all samples in batch for possible reanalysis.
Matrix spike samples: (Only prepared when samples with potential for matrix interferences are encountered)	One per batch	Control limits for recovery cannot exceed 100±20%	Select two additional samples and prepare fortified subsamples. Reanalyze all suspected samples in batch by the method of standard additions. Prepare three subsamples (unfortified, fortified with solution approximately equal to the endogenous concentration, and fortified with solution approximately twice the endogenous concentration.

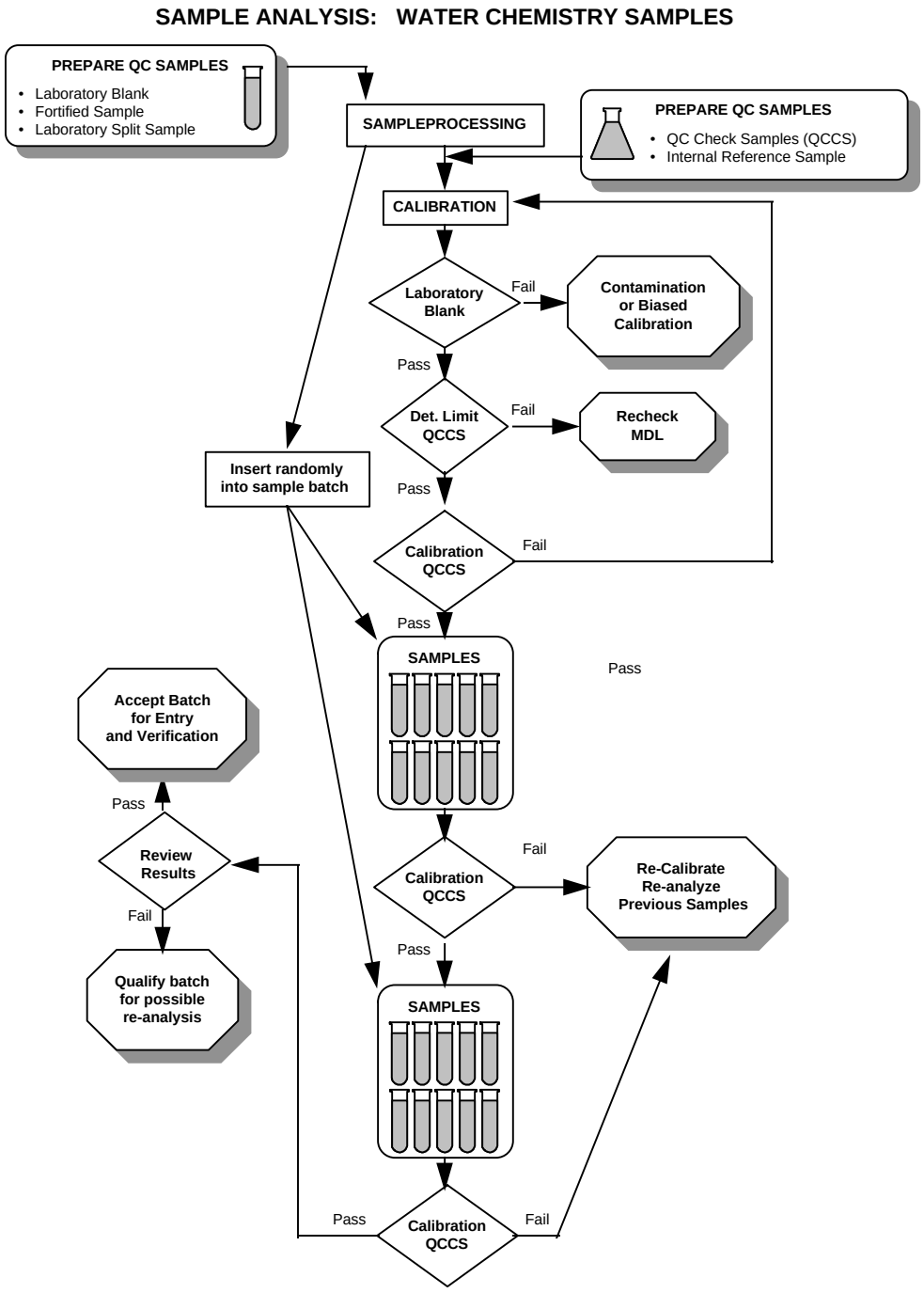

Figure 6-2. Analysis activities for water chemistry samples.

7.0 DATA REPORTING, REVIEW, AND MANAGEMENT

Checks made of the data in the process of review, verification, and validation are summarized in Table 7-1. Data reporting units and significant figures are given in Table 7-2. The Indicator Lead is ultimately responsible for ensuring the validity of the data, although performance of the specific checks may be delegated to other staff members.

Table 7-1. Data Validation Quality Control: Water Chemistry Indicator

Activity or Procedure	Requirements and Corrective Action
Range checks, summary statistics, and/or exploratory data analysis (e.g., box and whisker plots)	Correct reporting errors or qualify as suspect or invalid.
Review holding times	Qualify value for additional review
Ion balance: Calculate percent ion balance difference (%IBD) using data from cations, anions, pH, and ANC.	If total ionic strength # 100 µeq/L, %IBD # ±25%. If total ionic strength > 100 µeq/L, %IBD # ±10%. Determine which analytes, if any, are the largest contributors to the ion imbalance. Review suspect analytes for analytical error and reanalyze. If analytical error is not indicated, qualify sample to attribute imbalance to unmeasured ions. Reanalysis is not required. Flag= unacceptable %IBD Flag= %IBD outside acceptance criteria due to unmeasured ions
Conductivity check: Compare measured conductivity of each sample to a calculated conductivity based on the equivalent conductances of major ions in solution (Hillman et al., 1987).	If measured conductivity # 25 µS/cm, ([measured ! calculated] ÷ measured) # ±25%. If measured conductivity > 25 µS/cm, ([measured ! calculated] ÷ measured) # ±15%. Determine which analytes, if any, are the largest contributors to the difference between calculated and measured conductivity. Review suspect analytes for analytical error and reanalyze. If analytical error is not indicated, qualify sample to attribute conductivity difference to unmeasured ions. Reanalysis is not required.
Aluminum check: Compare results for organic monomeric aluminum, total monomeric aluminum, and total dissolved aluminum.	[organic monomeric] < [total monomeric] < [total dissolved]. Review suspect measurement(s) to confirm if analytical error is responsible for inconsistency.

(continued)

Table 7-1 (continued)

Activity or Procedure	Requirements and Corrective Action
ANC check: Calculate ANC based on pH and DIC. Compare to measured ANC	Review suspect measurements for samples with results outside of acceptance criteria. Determine if analytical error or non-carbonate alkalinity are responsible for lack of agreement.
Review data from QA samples (laboratory PE samples, and interlaboratory comparison samples)	Compare with results from other years to determine comparability. Determine impact and possible limitations on overall usability of data

Table 7-2. Data Reporting Criteria: Water Chemistry Indicator

Measurement	Units	No. Significant Figures	Maximum No. Decimal Places
Dissolved Oxygen	mg/L	2	1
Temperature	°C	2	1
pH	pH units	3	2
Carbon, dissolved inorganic	mg/L	3	2
Carbon, dissolved organic	mg/L	3	1
Acid neutralizing capacity	µeq/L	3	1
Conductivity	µS/cm at 25 °C	3	1
Aluminum (total dissolved, total monomeric, and organic monomeric)	µg/L	3	0
Calcium, magnesium, sodium, potassium, ammonium, chloride, nitrate, and sulfate	µeq/L	3	1
Silica	mg/L	3	2
Total phosphorus and total nitrogen	µg/L	3	0
Turbidity	NTU	3	0
True color	PCU	2	0
Total suspended solids	mg/L	3	1

The ion balance for each sample is computed using the results for major cations, anions, and the measured acid neutralizing capacity. The percent ion difference (%IBD) for a sample is calculated as:

$$\%IBD \quad \frac{(\,' \mathit{cations} \quad ' \mathit{anions}) \quad \mathit{ANC}}{\mathit{ANC} \quad ' \mathit{anions} \quad ' \mathit{cations} \quad 2[H\,]}$$

where ANC is the acid neutralization capacity, cations are the concentrations of calcium, magnesium, sodium, potassium, and ammonium, converted from mg/L to µeq/L, anions are chloride, nitrate, and sulfate (converted from mg/L to µeq/L), and H^+ is the hydrogen ion concentration calculated from the antilog of the sample pH. Factors to convert major ions from mg/L to µeq/L are presented in Table 7-3. For the conductivity check, equivalent conductivities for major ions are presented in Table 7-4.

Table 7-3. Constants for Converting Major Ion Concentrations from mg/L to µeq/L

Analyte	Conversion from mg/L to µeq/L[a]
Calcium	49.9
Magnesium	82.3
Potassium	25.6
Sodium	43.5
Ammonium	55.4
Chloride	28.2
Nitrate	16.1
Sulfate	20.8

[a] Measured values are multiplied by the conversion factor.

Table 7-4. Factors to Calculate Equivalent Conductivities of Major Ions[a]

Ion	Equivalent Conductance per mg/L (µS/cm at 25 ɛC)	Ion	Equivalent Conductance per mg/L (µS/cm at 25 ɛC)
Calcium	2.60	Nitrate	1.15
Magnesium	3.82	Sulfate	1.54
Potassium	1.84	Hydrogen	3.5×10^5 [b]
Sodium	2.13	Hydroxide	1.92×10^5 [b]
Ammonium	4.13	Bicarbonate	0.715
Chloride	2.14	Carbonate	2.82

[a] From Hillman et al. (1987).
[b] Specific conductance per mole/L, rather than per mg/L.

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PHYSICAL HABITAT QUALITY INDICATOR (STREAMS)

1.0 INTRODUCTION

Naturally occurring differences in physical habitat structure and associated hydraulic characteristics among surface waters contributes to much of the observed variation in species composition and abundance within a zoogeographic province. Structural complexity of aquatic habitats provides the variety of physical and chemical conditions to support diverse biotic assemblages and maintain long-term stability. Anthropogenic alterations of riparian physical habitat, such as channel alterations, wetland drainage, grazing, agricultural practices, weed control, and streambank modifications such as revetments or development, generally act to reduce the complexity of aquatic habitat and result in a loss of species and ecosystem degradation.

For EMAP, indicators derived from data collected about physical habitat quality will be used to help explain or diagnose stream condition relative to biological response and trophic state indicators. Specific groups of physical habitat attributes important in stream ecology include: channel dimensions, gradient, substrate; habitat complexity and cover; riparian vegetation cover and structure; anthropogenic alterations; and channel-riparian interaction (Kaufmann, 1993). Overall objectives for this indicator are to develop quantitative and reproducible indices, using both multivariate and multimetric approaches, to classify streams and to monitor biologically relevant changes in habitat quality and intensity of disturbance.

2.0 SAMPLING DESIGN

As the physical habitat indicator is based on field measurements and observations, there is no sample collection associated with this indicator. Field crews are provided with 1:24,000 maps with the midpoint (index site) of the stream reach marked. At EMAP sites, eleven cross-sectional measurement sites are spaced at equal intervals proportional to baseflow channel width, thereby scaling the sampling reach length and resolution in proportion to stream size. A systematic spatial sampling design is used to minimize bias in the selection of the measurement sites. Additional measurements are made at equally spaced intervals between the cross-sectional sites. A “rapid” assessment of habitat quality of the entire sampling reach is conducted based on the Rapid Bioassessment Protocol (RBP; Plafkin et al, 1989).

3.0 SAMPLING METHODOLOGIES

Field Measurements: Field measurements, observations, and associated methodology for the EMAP protocol are summarized in Table 3-1; methodology for the RBP is described in Plafkin et al, 1989. Detailed procedures for completing both protocols are provided in the field operations manual; equipment and supplies required are also listed. All measurements and observations are recorded on standardized forms which are later entered in to the central EMAP surface waters information management system at WED-Corvallis.

There are no sample collection nor laboratory analyses associated with the physical habitat measurements.

Table 3-1. Field Measurement Methods: Physical Habitat Indicator

Variable or Measurement	Units	QA Class	Summary of Method	References
THALWEG PROFILE				
Thalweg depth	cm	C	Measure maximum depth at 100-150 points along reach with surveyor's rod and meter stick	
Wetted width	0.1m	C	Measure wetted width with meter stick or measureing tape on perpendicular line to mid-channel line	
Habitat class	none	N	Visually estimate channel habitat using defined class descriptions	Frissel et al, 1986
WOODY DEBRIS TALLY				
Large woody debris	number of pieces	N	Visually estimate amount of woody debris in baseflow channel using defined class descriptions	Robison and Beschta, 1990
CHANNEL AND RIPARIAN CROSS-SECTIONS				
Slope and bearing	percent/ degrees	C	Backsight between cross-section stations using clinometer, rangefinder compass, and tripod	Stack, 1989; Robison and Kaufmann, in prep.
Substrate size	mm	C	At 5 points on cross section, estimate size of one selected particle using defined class descriptions	Wollman, 1954; Bain et al, 1985; Plafkin et al, 1989
Bank angle	degrees	N	Use clinometer and surveyors rod to measure angle	Platts et al, 1983
Bank incision	0.1m	N	Visually estimate height from water surface to first terrace of floodplain	
Bank undercut	cm	N	Measure horizontal distance of undercut	
Bankful width	0.1m	N	Measure width at top of bankful height	
Bankful height	0.1m	N	Measure height from water surface to estimated water surface during bankful flow	
Canopy cover	points of inter-section	C	Count points of intersection on densiometer at specific points and directions on cross-section	Lemmon, 1957; Mulvey et al, 1992
Riparian vegetation structure	percent	N	Observations of ground cover, understory, and canopy types and coverage of area 5 m on either side of cross section and 10 m back from bank	
Fish cover, algae, macrophytes	percent	C	Visually estimate in-channel features 5 m on either side of cross section	
Human influence	none	C	Estimate presence/absence of defined types of anthropogenic features	

C = critical, N = non-critical quality assurance classification. **(Continued)**

Table 3-1. Continued

Variable or Measurement	Units	QA Class	Summary of Method	References
STREAM DISCHARGE				
Discharge	m/s or L/min.	N	Velocity-Area method, Portable Weir method, timed bucket discharge method	Linsley et al, 1982

C = critical, N = non-critical quality assurance classification.

4.0 QUALITY ASSURANCE OBJECTIVES

Measurement data quality objectives (measurement DQOs or MQOs) are given in Table 4-1. General requirements for comparability and representativeness addressed in Part I, Section 4. The MQOs given in Table 4-1 represent the maximum allowable criteria for statistical control purposes. Precision is determined from results of revisits by a different crew (field measurements) and by duplicate measurements by the same individual on a different day or by a different individual (map-based measurements).

The completeness objectives are established for each measurement *per site type* (e.g., EMAP sites, revisit sites). Failure to achieve the minimum requirements for a particular site type results in regional population estimates having wider confidence intervals. Failure to achieve requirements for repeat and annual revisit samples reduces the precision of estimates of index period and annual variance components, and may impact the representativeness of these estimates because of possible bias in the set of measurements obtained.

Table 4-1. Measurement Data Quality Objectives: Physical Habitat Indicator

Variable or Measurement	Precision	Accuracy	Completeness
Field Measurements and Observations	±10%	NA	90%
Map-Based Measurements	±10%	NA	100%

NA = not applicable

5.0 QUALITY CONTROL PROCEDURES: FIELD OPERATIONS

Specific quality control measures are listed in Table 5-1 for field measurements and observations.

Table 5-1. Field Quality Control: Physical Habitat Indicator

Check Description	Frequency	Acceptance Criteria	Corrective Actions
Check totals for cover class categories (vegetation type, fish cover)	Each transect	Sum must be reasonable	Repeat observations
Check completeness of thalweg depth measurements	Each site	Depth measurements for all sampling points	Obtain best estimate of depth where actual measurement not possible
Check calibrate of current velocity meter	Prior to each use	Specific to instrument	Adjust and recalibrate, use alternative method

6.0 QUALITY CONTROL PROCEDURES: LABORATORY OPERATIONS

There are no laboratory operations associated with this indicator.

7.0 DATA MANAGEMENT, REVIEW, AND VALIDATION

Checks made of the data in the process of review, verification, and validation are summarized in Table 7-1. The Indicator Lead is ultimately responsible for ensuring the validity of the data, although performance of the specific checks may be delegated to other staff members. All raw data (including all standardized forms and logbooks) are retained in an organized fashion for seven years or until written authorization for disposition has been received from the EMAP Diractor.

Table 7-1. Data Validation Quality Control: Physical Habitat Indicator

Check Description	Frequency	Acceptance Criteria	Corrective Action
Compare field estimates to those determined from recent aerial photographs	Each stream for which aerial photograph is available	Estimates should be within 10 percent	Flag data
Estimate precision of measurements based on repeat visits by different crews	Each revisit stream	Measurements should be within 10 percent	Review data for reasonableness; Determine if acceptance criteria need to be modified

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STREAM PERIPHYTON INDICATOR

1.0 INTRODUCTION

Periphyton are the algae, fungi, bacteria, and protozoa associated with substrates in aquatic habitats. These organisms exhibit high diversity and are a major component in energy flow and nutrient cycling in aquatic ecosystems. Many characteristics of periphyton community structure and function can be used to develop indicators of ecological conditions in streams. Periphyton are sensitive to many environmental conditions, which can be detected by changes in species composition, cell density, ash free dry mass (AFDM), chlorophyll, and enzyme activity (e.g., alkaline and acid phosphatase). Each of these characteristics may be used, singly or in concert, to assess EMAP surface waters societal values of biological integrity and trophic condition.

A hierarchical framework is being used in the development of the periphyton indices of stream condition. The framework involves the calculation of composite indices for biotic integrity, ecological sustainability, and trophic condition. The composite indices will be calculated from measured or derived first-order and second-order indices. The first-order indices include species composition (richness, diversity), cell density, AFDM, chlorophyll, and enzyme activity, which individually are indicators of ecological condition in streams. Second-order indices will be calculated from periphyton characteristics, such as the autotrophic index (Weber, 1973), community similarity compared to reference sites, and autecological indices (e.g., Lowe, 1974; Lange-Bertalot, 1979; Charles, 1985; Dixit et al, 1992).

The metrics associated with the indicator are summarized in Table 1-1.

Table 1-1. Proposed Indicators of Condition and Associated Metrics: Stream Periphyton Indicator

Indicator and Description	Associated Metrics
Species composition	Species diversity, evenness, autecological indices
Cell density (no./cm^2	Abundance
Chlorophyll (µg Chl./cm^2)	Standing crop, productivity, trophic status, autotrophic index
Standing stock (mg AFDM/cm^2)	Productivity, trophic status
Phosphatase activity (mmol/g AFDM)	Community activity (function)

2.0 SAMPLING DESIGN

For the MAIA regional stream survey, Index samples for all types of periphyton samples are collected from all stream reaches identified in the Tier II sample selected for EMAP and EMAP reference sites. Periphyton samples are not collected from sites selected specifically for the Oregon stream pilot survey.

The plot design for periphyton is based on stratification by major macrohabitat type (erosional versus depositional). Periphyton samples are collected from each macrohabitat type at each of the designated transects within the stream reach. Erosional macrohabitats are composited into a single sample, as are depositional macrohabitats. The index sampling design is illustrated in Figure 2-1.

3.0 SAMPLING AND ANALYTICAL METHODOLOGIES

Sample Collection: Within each stream reach, a sampling site is selected at random at each of nine cross-sectional transects established at equal distances along the reach. At each transect site, an erosional or depositional sample is collected. Erosional samples are composited to produce one erosional index sample; depositional samples are composited to produce one depositional index sample. Detailed procedures for collecting periphyton from each type of macrohabitat are described in the field operations manual.

Analysis: Four types of periphyton samples are prepared from each index sample: an ID/enumeration sample, a chlorophyll sample, a biomass sample, and a sample for acid/alkaline phosphatase analysis. Analytical methods are based on standard ASTM or APHA methodologies. Analytical methods for the periphyton indicator are summarized in Table 3-1.

4.0 QUALITY ASSURANCE OBJECTIVES

Measurement data quality objectives (measurement DQOs or MQOs) are given in Table 4-1. General requirements for comparability and representativeness addressed in Part I, Section 4. The MQOs given in Table 4-1 represent the maximum allowable criteria for statistical control purposes. Detection limits are only applicable to chlorophyll determinations and are estimated from replicate determinations of a low-level standard using Equation 4-1 (see Part I, Section 4). This is not a true method detection limit detection limit, as the low-level standard used is not subjected to the entire preparation and analysis process. For biomass estimates, the "detection limit" is defined based on the required sensitivity of the analytical balance. In addition, field blank samples are used to determine background levels of chlorophyll or related compounds introduced during sample filtration, transport, extraction, and analysis

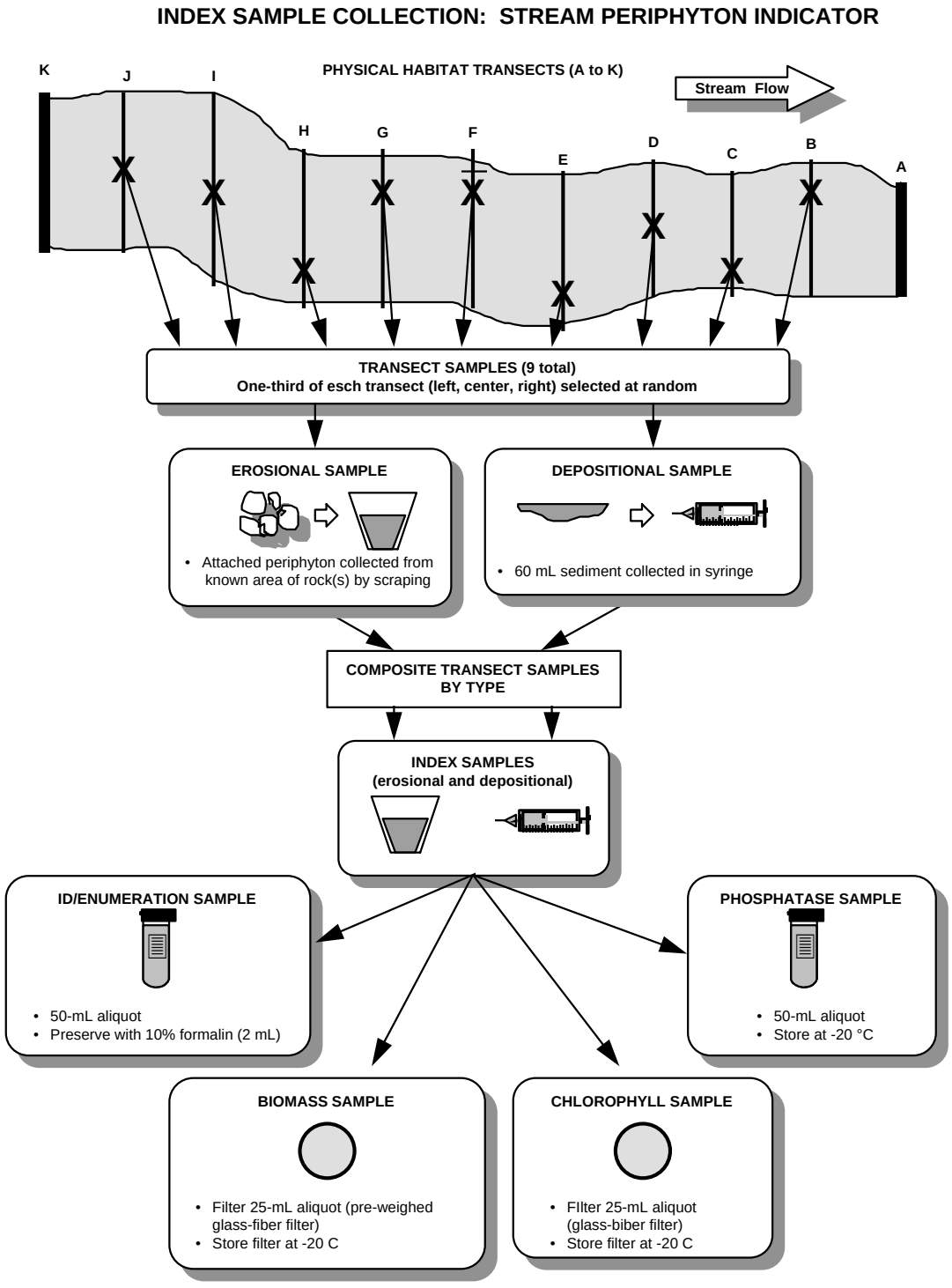

Figure 2-1. Index sampling design for the stream periphyton indicator.

Table 3-1. Analytical Methodologies: Stream Periphyton Indicator

Sample Type and Measurements	Expected Range and/or Units	Summary of Method	References
ID/Enumeration: Species Composition Relative Density	species/sample cells/mL or cells/cm^2	Quantitative sample collected and preserved (formalin) in field; analysis by Palmer cell counts (200 organisms) using either strip count or random field technique	Weitzel (1979); APHA (1991)
Chlorophyll: Chlorophyll *a*	1 to 100 µg/cm^2	Quantitative filtration (glass fiber) in field; extraction of filter into acetone; analysis by spectrophotometry (monochromatic)	APHA 10200 H-2; APHA (1991)
Biomass: Ash-free Dry Mass (AFDM)	mg/cm^2	Quantitative filtration (leached, combusted, and pre-weighed glass fiber) in field; gravimetric analysis	APHA (1991)
Alkaline/Acid Phosphatase	mmol/g AFDM mmol/cm^2	Spectrophotometric determination	Sayler et al (1979)

For ID/enumeration samples, taxonomic accuracy of species composition data and precision of enumeration data is estimated from repeated determinations of individual samples by different individuals. Taxonomic accuracy is estimated as described in Part I, Section 2. For chlorophyll determinations, precision and relative bias are estimated from repeated analysis of a PE sample prepared from a sample of natural lake or stream water. Precision is also estimated from field replicate samples analyzed in different analytical batches. Precision of biomass determinations is estimated from measurements of standard weights over different analytical batches, or from field replicate samples weighed on different days.

The completeness objectives are established for each measurement *per site type* (e.g., probability sites, revisit sites, etc.). Failure to achieve the minimum requirements for a particular site type results in regional population estimates having wider confidence intervals. Failure to achieve requirements for repeat and annual revisit samples reduces the precision of estimates of index period and annual variance components, and may impact the representativeness of these estimates because of possible bias in the set of measurements obtained.

Table 4-1. Measurement Data Quality Objectives: Stream Periphyton Indicator

Variable or Measurement	Detection Limit	Precision	Accuracy	Completeness
Species Composition	NA	NA	±90%	90%
Relative Density	NA	±30%	NA	90%
Chlorophyll *a*	1 µg/L[a]	±1 µg/cm^2 or ±20%[b]	±1 µg/cm^2 or ±10%[b]	90%
Ash-free Dry Mass	0.1mg/cm^2	±0.1 mg/cm^2	0.1 mg/cm^2	90%
Alkaline/Acid Phosphatase	0.01 mmol	± 0.01 mmol	0.01 mmol	90%

NA = not applicable
[a] Detection limit estimated as the one-sided 99 percent confidence interval based at least seven measurements of a low-level standard subjected to laboratory preparation and analysis.
[b] Above transition value of 5 µg/cm^2, precision and bias are expressed in relative terms.

5.0 QUALITY CONTROL PROCEDURES: FIELD OPERATIONS

Specific quality control measures are listed in Table 5-1 for field operations. Collection and handling procedures for water samples to ensure compliance with these requirements are documented in the field operations manuals.

6.0 QUALITY CONTROL PROCEDURES: LABORATORY OPERATIONS

ID/Enumeration Samples: The general processing and analysis scheme for ID/enumeration samples is depicted in Figure 6-1. Quality control activities associated with receiving, preparing, and analyzing of ID/enumeration samples are presented in Table 6-1. Information regarding QC sample or measurement requirements and corrective actions for ID/enumeration samples are summarized in Table 6-2.

Table 5-1. Field Quality Control: Stream Periphyton Indicator

QC Activities	Requirements
Sample Container and Filters Preparation and Handling	Rinse all sample containers and soak for 48 h with ASTM Type II reagent water. Chlorophyll samples: Keep glass fiber filters in dispenser placed in sealed plastic bag until use. Inspect filtration equipment before each use for damage or contamination. Rinse filtration chamber with ASTM Type II reagent water daily before use. Biomass samples: Prepare filters for use by combusting (30 min at 525 °C), desiccating, re-hydrating, then drying (60 °C for 24 hours). Weigh to nearest 0.01 mg. Place in sealed container labelled with weight. Activity samples: Clean sample containers. Rinse syringe with ASTM Type II reagent water before subsampling.
Contamination prevention	All containers for individual site sealed in plastic bags until use Avoid external sources of contamination (e.g., dust, dirt, or mud) that are present at streamside. Handle glass fiber filters with clean forceps only.
Sample processing (field)	Chlorophyll Samples: Use 0.45 µm nominal pore size glass fiber filter (Whatman GF/F or equivalent). Conduct filtration procedure in subdued light. Filtration equipment (and filters) are rinsed with deionized water and portions of sample before use. The volume of sample filtered (generally 50 mL) must be measured accurately (±1 mL) with a graduated cylinder. During filtration, the vacuum pressure cannot exceed 7 pounds per square inch (psi)., or a new sample is prepared. Biomass Samples: Filtration equipment (and filters) are rinsed with deionized water and portions of sample before use. The volume of sample filtered (generally 50 mL) must be measured accurately (±1 mL) with a graduated cylinder. During filtration, the vacuum pressure cannot exceed 7 pounds per square inch (psi)., or a new sample is prepared.
Minimum volumes	ID/Enumeration sample= 50 mL Chlorophyll sample= 25 mL (filtered). Biomass sample= 25 mL (filtered). Activity Sample= 50 mL .
Storage Conditions (from collection until receipt at laboratory)	ID/Enumeration samples: Preserve w/ 2 mL 10% formalin. Chlorophyll samples: Store filter in darkness at -20 °C. Biomass samples: Store filter at -20 °C. Activity Samples: Store in darkness at -20 °C
Shipping requirements	Maintain chlorophyll, biomass, and activity samples at -20 °C until shipment or transport to laboratory. Ship or transport in UN-approved containers that maintain required storage conditions. NOTE: Transport or shipment of formalin-preserved samples and samples preserved with dry ice are may be considered hazardous materials, requiring special labelling and manifesting.

SAMPLE PROCESSING AND ANALYSIS: PERIPHYTON ID/ENUMERATION SAMPLES

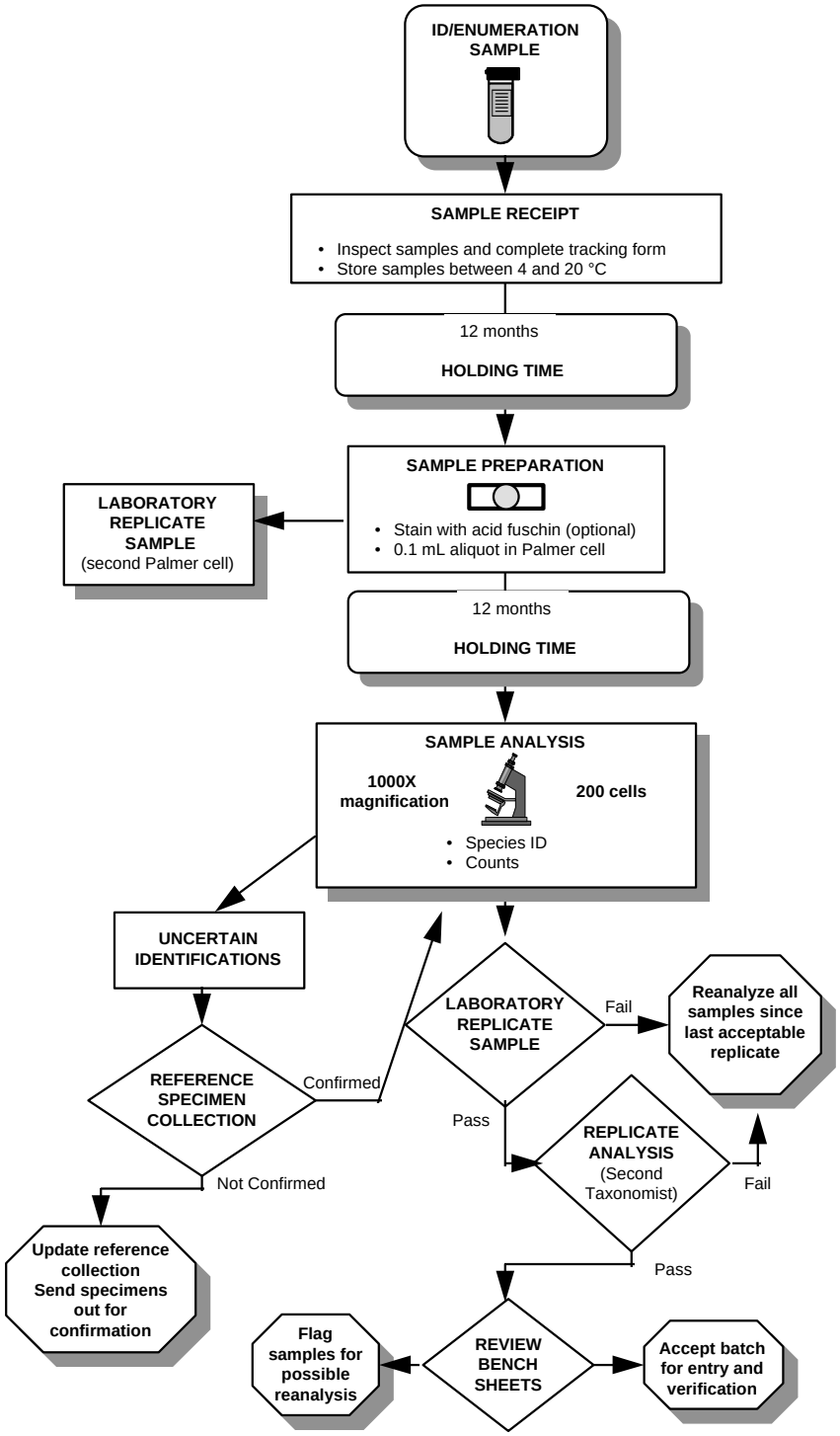

Figure 6-1. Processing and analysis of stream periphyton identification/enumeration samples.

Table 6-1. Laboratory Quality Control: Stream Periphyton ID/Enumeration Samples

Quality Control Activity	Description and Requirements	Corrective Action
Sample Receipt		
Sample Storage	Store samples in well-ventilated area between 4 and 20 °C. Monitor temperature weekly. Check state of preservation monthly.	Qualify sample as suspect for all analyses
Holding times	Formalin-preserved samples should be stained or analyzed within 12 months of collection.	Qualify samples
Sample Processing:		
Sample Preparation	Staining (acid fuschin) is optional. After staining, store samples in well-sealed vials. Inspect frequently for loss of fluid.	Qualify samples as suspect or lost.
Holding Time after processing	12 months for stained samples	
Sample Analysis:		
Reference/ voucher specimens	Prepare permanent mounts of all uncertain or new taxa as encountered. Prepare by persulfate oxidation of sample. Use high-resolution mounting media (Hyrez or equivalent)	

Chlorophyll Samples: Figure 6-2 illustrates the general scheme for processing chlorophyll samples and Figure 6-3 depicts analysis of periphyton chlorophyll samples. Quality control activities associated with receiving, preparing, and analyzing of chlorophyll samples are presented in Table 6-3. Information regarding QC sample requirements and corrective actions are summarized in Table 6-4.

Table 6-2. Quality Control Samples: Stream Periphyton ID/Enumeration Samples

QC Sample Type and Description	Frequency	Acceptance Criteria	Corrective Action
Pipette Check Sample (transfer volume): Three aliquots of DI water collected by transfer pipette are weighed.	Daily.	Control limits: Mean weight # 0.1±0.01 g	Recalibrate pipette before proceeding with any sample analyses. Reestablish statistical control by analyzing three successive sets of water aliquots.
ID/Enumeration QCCS: Palmer cell sample selected at random. Sample is re-analyzed by experienced taxonomist.	At least three samples per technician or 10% of samples divided evenly among technicians (whichever is larger)	Control limits: Taxonomic accuracy $ 90%	All samples analyzed by technician since last acceptable QCCS determination are evaluated by senior taxonomist for possible re-analysis. Demonstrate re-establishment of technician by three successful QCCS
Internal Reference Sample (identification): Specimen that has been confirmed by taxonomic expert	As needed	Not Applicable	Qualify identification as suspect. Send specimen to taxonomic expert for confirmation.
Laboratory Split Sample: (Identification and enumeration) Select sample at random and prepare two Palmer cell samples for identification and enumeration. Analyze using different technicians or on different days (same technician)	7 samples or 10% of samples (whichever is larger)	Control Limits: Taxonomic accuracy $ 90%	Prepare and analyze split prepared from second randomly selected sample. Check preparation of split sample. Qualify and evaluate all samples since last acceptable split sample determination for possible reanalysis.

Biomass Samples: Figure 6-4 illustrates the general scheme for processing and analysis of periphyton biomass samples. Quality control activities associated with receiving, preparing, and analyzing of biomass samples are presented in Table 6-5. Information regarding QC sample requirements and corrective actions are summarized in Table 6-6.

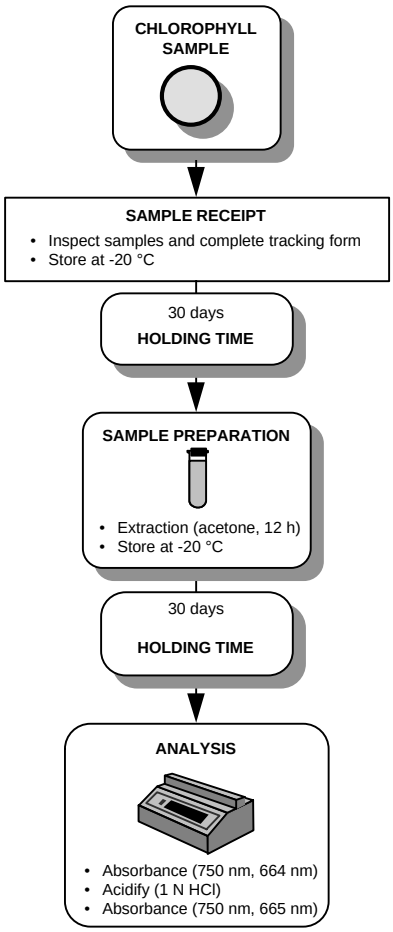

Figure 6-2. Chlorophyll sample processing for the stream periphyton indicator.

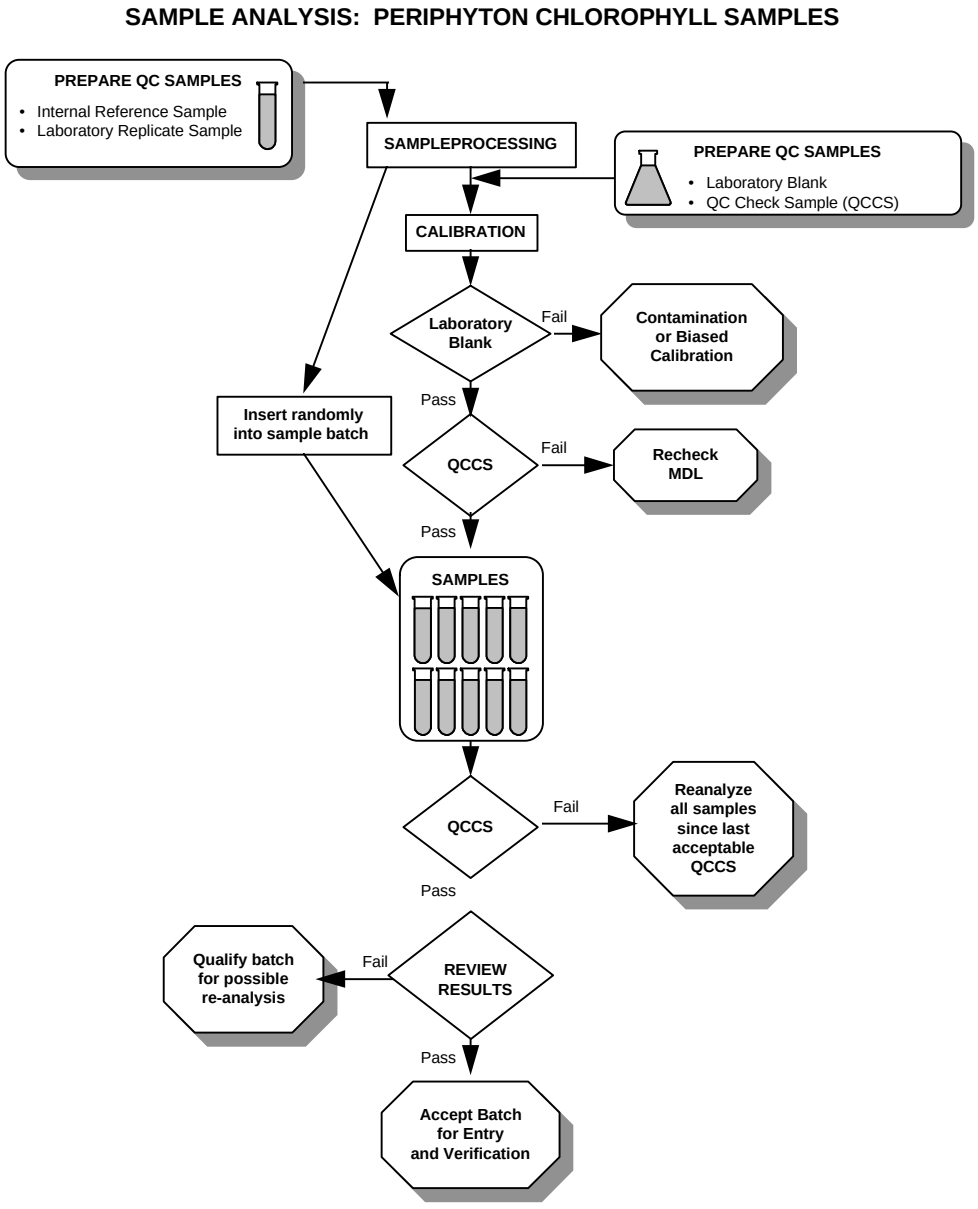

Figure 6-3. Chlorophyll sample analysis for the stream periphyton indicator.

Table 6-3. Laboratory Quality Control: Stream Periphyton Chlorophyll Samples

Quality Control Activity	Description and Requirements	Corrective Action
Sample Receipt		
Sample custody	Assign internal sample ID to each samples. Enter sample label and tracking information into LIMS	Confirm all samples received and stored are logged into LIMS
Sample Storage	Store samples in darkness at !20 °C. Monitor temperature daily.	Qualify sample as suspect for all analyses
Holding times (unprocessed samples)	30 days	Qualify samples
Sample Processing:		
Sample Preparation	Volume of acetone used must be dispensed and recorded accurately. Steep extract in darkness at 4 °C for 12 hours	Qualify samples as suspect or lost.
Holding Time after processing	30 days for sample extracts	Qualify samples.

Activity Samples: Figure 6-5 illustrates the general scheme for processing phosphatase samples and Figure 6-6 depicts analysis of periphyton phosphatase samples. Quality control activities associated with receiving, preparing, and analyzing of activity samples are presented in Table 6-7. Information regarding QC sample requirements and corrective actions are summarized in Table 6-8.

Table 6-4. Quality Control Samples: Stream Periphyton Chlorophyll Samples

QC Sample Type and Description	Frequency	Acceptance Criteria	Corrective Action
Laboratory Blank Sample: Reagent Blank: Aliquot of acetone is processed through tissue grinder.	Once per batch prior to sample analysis.	Control limits < ±Detection limit	Check calibration for possible bias. Check reagents and preparation equipment for possible contamination.
Quality Control Check Sample (QCCS): Chlorophyll standard in extract form prepared so concentration is approximately four to six times the required MDL	Before and after sample analyses, after every 7 to 10 routine samples	Control limits < ±Detection limit	Confirm achieved MDL by repeated analysis of appropriate standard solution. Evaluate affected samples for possible re-analysis.
Internal Reference Sample: Prepared as a series of replicate samples from a single source of lake or stream water and characterized by repeated measurement before use.	Once per batch	Control limits < precision objective: Mean value < bias objective (based on target value of sample)	Analyze standard in next batch to confirm suspected imprecision or bias. Evaluate calibration standards and reference sample for contamination and preparation error. Correct before any further analyses of routine samples are conducted. Reestablish control by three successive reference sample measurements which are acceptable. Qualify all sample batches analyzed since the last acceptable reference standard measurement for possible reanalysis.
Laboratory Split Sample: Prior to processing, select at least one routine sample in each batch at random and prepare two extracts for analysis.	One per batch	Control limits # than precision objective	If mean value is below MDL Prepare and analyze split from different sample (volume permitting). Review precision of QCCS measurements for batch. Check preparation of split sample. Qualify all samples in batch for possible reanalysis.

SAMPLE ANALYSIS: PERIPHYTON BIOMASS SAMPLES

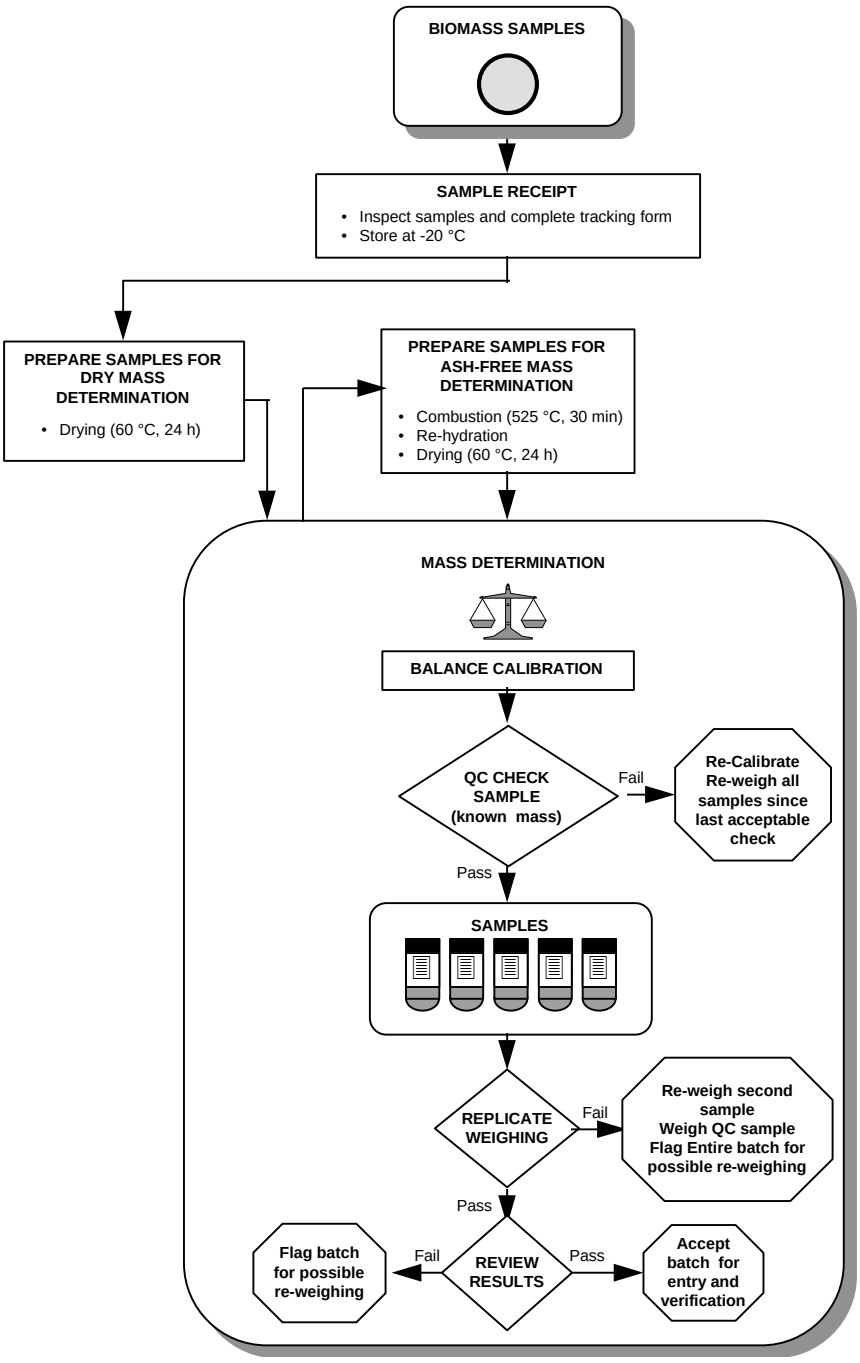

Figure 6-4. Biomass analysis for the stream periphyton indicator.

Table 6-5. Laboratory Quality Control: Stream Periphyton Biomass Samples

Quality Control Activity	Description and Requirements	Corrective Action
Sample Receipt		
Sample custody	Assign internal sample ID to each samples. Enter sample label and tracking information into LIMS	Confirm all samples received and stored are logged into LIMS
Sample Storage	Store samples at !20 °C. Monitor temperature daily.	Qualify sample as suspect for all analyses
Holding times (unprocessed samples)	30 days	Qualify samples
Sample Processing:		
Sample Preparation	Drying conditions: 60 °C for 24 hours. Combustion conditions: 525 °C for 30 min. Use desiccator to cool. Use reagent water to re-hydrate. Handle filters with forceps only.	Qualify suspect samples

Table 6-6. Quality Control Samples: Stream Periphyton Biomass Samples

QC Sample Type and Description	Frequency	Acceptance Criteria	Corrective Action
Quality Control Check Sample (QCCS): Standard weight of representative mass that is not used to calibrate balance	Once per batch	Control limits: < precision and bias objectives	Check calibration and recalibrate if necessary. Qualify all samples analyzed since last acceptable QCCS determination for possible re-analysis.
Laboratory Split Sample: Select at one routine sample in each batch at random. Repeat weighing at end of each step of sample analysis	One per batch	Control limits # than precision objective	Conduct split sample determination on second sample. Review precision of QCCS measurements for batch. Check preparation of filters. Qualify and evaluate all samples in batch for possible reanalysis.

SAMPLE PROCESSING: PERIPHYTON PHOSPHATASE SAMPLES

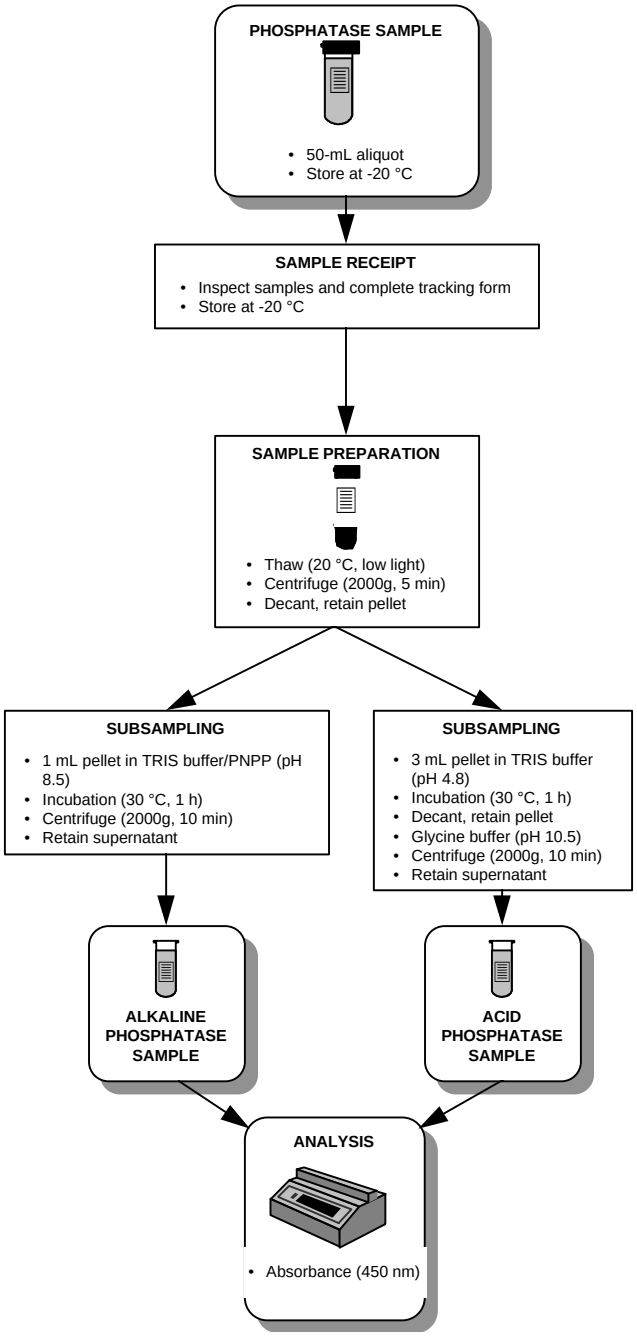

Figure 6-5. Sample processing for the stream periphyton phosphatase samples.

SAMPLE ANALYSIS: PERIPHYTON PHOSPHATASE SAMPLES

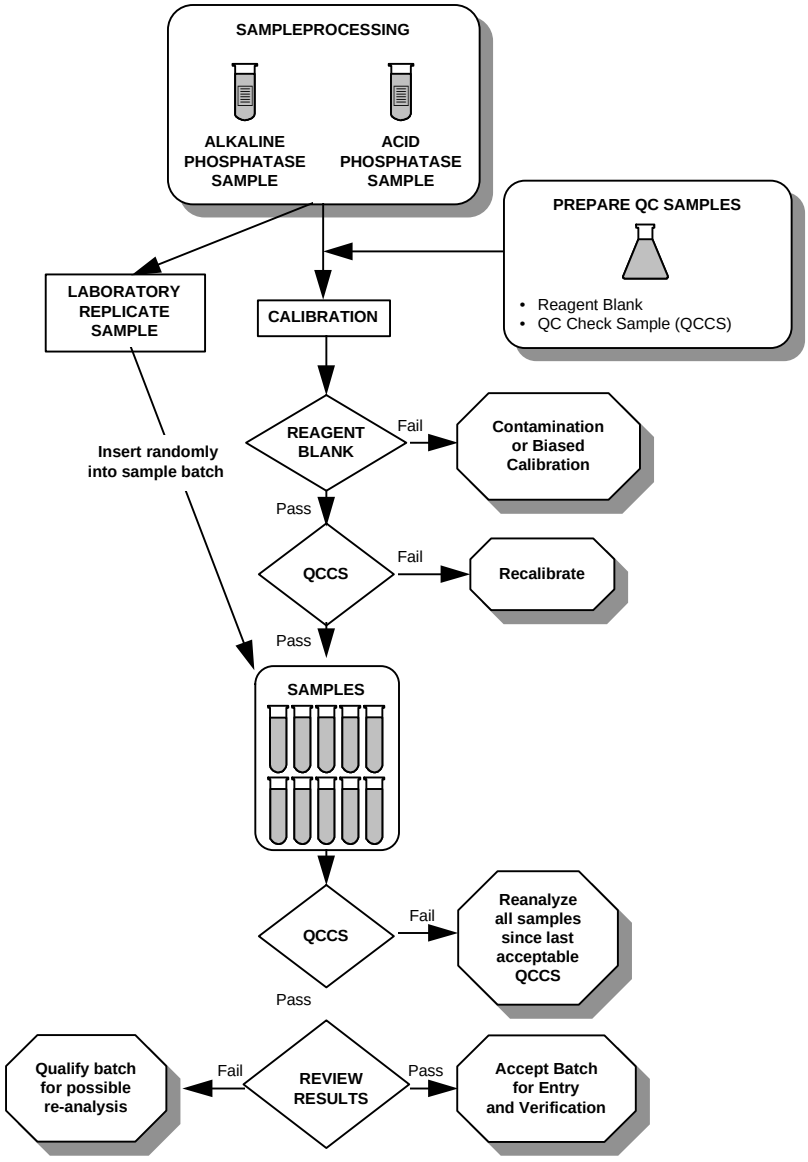

Figure 6-6. Sample analysis for the stream periphyton phosphatase samples.

Table 6-7. Laboratory Quality Control: Stream Periphyton Activity Samples

Quality Control Activity	Description and Requirements	Corrective Action
Sample Receipt		
Sample custody	Assign internal sample ID to each samples. Enter sample label and tracking information into LIMS	Confirm all samples received and stored are logged into LIMS
Sample Storage	Store samples in darkness at ¦20 °C. Monitor temperature daily.	Qualify sample as suspect for all analyses
Holding times (unprocessed samples)	90 days	Qualify samples
Sample Processing:		
Holding Time after processing	90 days for Processed samples	Qualify samples.

Table 6-8. Quality Control Samples: Stream Periphyton Activity Samples

QC Sample Type and Description	Frequency	Acceptance Criteria	Corrective Action
Detection Limit QCCS: Prepared so concentration is approximately four to six times the required MDL .	Before and after sample analyses, after every 7 to 10 routine samples	Control limits < ±Detection limit	Confirm achieved MDL by repeated analysis of appropriate standard solution. Evaluate affected samples for possible re-analysis.
Calibration QCCS: Prepared so concentration between 25 percent and 75 percent of the calibration range	Before and after sample analyses	Control limits < precision objective: Mean value < bias objective	Repeat QCCS analysis. Recalibrate and analyze QCCS. Reanalyze all routine samples (including PE and field replicate samples) analyzed since the last acceptable QCCS measurement.
Internal Reference Sample: (Suggested if available) Standard Reference Materials (SRMs) or Certified Reference Materials (CRMs) that are traceable to a standards organization. Alternatively, non-traceable but well-characterized samples can be utilized.	One analysis in a minimum of five separate batches	Control limits < precision objective: Mean value < bias objective	Analyze standard in next batch to confirm suspected imprecision or bias. Evaluate calibration and QCCS solutions and standards for contamination and preparation error. Correct before any further analyses of routine samples are conducted. Reestablish control by three successive reference standard measurements which are acceptable. Qualify all sample batches analyzed since the last acceptable reference standard measurement for possible reanalysis.

7.0 DATA REPORTING, REVIEW, AND MANAGEMENT

Checks made of the data in the process of review, verification, and validation are summarized in Table 7-1. Data reporting units and significant figures are given in Table 7-2. The Indicator Lead is ultimately responsible for ensuring the validity of the data, although performance of the specific checks may be delegated to other staff members.

Table 7-1. Data Validation Quality Control: Stream Periphyton Indicator

Activity or Procedure	Requirements and Corrective Action
Range checks, summary statistics, and/or exploratory data analysis (e.g., box and whisker plots)	Correct reporting errors or qualify as suspect or invalid
Review holding times	Qualify value for additional review
Review data from QA samples (field blanks, PE samples, and interlaboratory comparison samples)	Compare with results from other years to determine comparability. Determine impact and possible limitations on overall usability of data
Summarize and review replicate sample data (repeat visits, annual revisits).	Identify replicate samples with large variance. Determine if analytical error or visit-specific phenomenon is responsible.

Table 7-2. Data Reporting Criteria: Stream Periphyton Indicator

Measurement	Units	Max. No. Decimal Places	No. Significant Figures
Species Density	cells/mL or cells/cm^2	0	
Chlorophyll	µg/L or µg/cm^2	4	
Ash-free Dry Mass	mg/cm^2	2	
Activity	mmol/g AFDM or mmol/cm^2	2	

8.0 REFERENCES

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BENTHIC INVERTEBRATES INDICATOR (STREAMS)

1.0 INTRODUCTION

The benthic invertebrate assemblage found in sediments and on substrates of streams reflect the biological integrity of the benthic community. The response of benthic communities to various stressors can often be used to determine the type of stressor and to monitor trends (Klemm et al, 1990). The overall objectives of the benthic invertebrate indicator are to detect stresses on community structure in wadeable streams and to assess and monitor the relative severity of those stresses. The EMAP benthic invertebrate indicator procedures are based on the Rapid Bioassessment Protocol III (RBP; Plafkin et al, 1989).

Specific research questions and hypotheses to be addressed from this year's activities are listed in Table 1-1. The metrics associated with the indicator are summarized in Table 1-2.

Table 1-1. Research Questions and Hypotheses: Benthic Invertebrates Indicator (Streams)

EMAP Design Evaluation	Obtain estimates of variance components from revisit sites.
Indicator Development and Evaluation	Determine optimal subsampling and enumeration protocol for taxa richness and relative abundance measurements Determine the relative importance of the riffle and the pool composite samples in assessing stream condition Pilot different approaches to collecting a representive index sample from non-wadeable streams and rivers.
Other Evaluation	Compare results of composite riffle and pool samples with a single composite containing both riffle and pool organisms and with samples from three, randomly selected sampling locations.

Table 1-2. Proposed Indices of Condition and Associated Metrics: Benthic Invertebrates Indicator

Indicator and Description	Associated Metrics
Stream Benthic Integrity Index (BII) determined as composite score of values assigned to defined ranges of metrics; ranges independently assigned for riffle and for pool composite samples	HBI, No. of Taxa, No. of Individuals/Taxon, %Intolerant Taxa, %non-insects, %chironomids, % oligo. and leeches, %Ind. Dominant Taxon, %EPT Taxa, and EPT Index
Biological Condition	Ratio of BII for Reference Station/Study Station or defined range of total BII for Study Station

2.0 SAMPLING DESIGN

Benthic invertebrates are collected at randomly selected sampling locations on the cross-sectional transects established along the stream reach. Two index samples are collected, one a composite of invertebrates collected from pool areas and the other a composite of invertebrates collected from riffles. The index sampling design is illustrated in Figure 2-1.

3.0 SAMPLING AND ANALYTICAL METHODOLOGIES

Sample Collection: Benthic invertebrates are collected from an approximately 20 cm^2 area randomly selected at each of the interior nine cross-sectional transects. Samples collected from riffle areas using a modified kick-net procedures are composited together, as are samples collected from pool areas. Samples are field-processed to remove large detritus and preserved in formalin. Detailed sampling and processing procedures are described in the field operations manual.

Analysis: Preserved composite samples are sorted, enumerated, and invertebrates identified to the lowest possible taxonomic level using specified standard keys and references. Analytical methods are based on standard limnological practices. Detailed procedures are contained in the laboratory operations manual and cited references. There is no maximum holding time associated with preserved benthic invertebrate samples. For operational purposes, analyses should be completed within one year of sample collection.

Table 3-1 summarizes field and analytical methods for the benthic invertebrates indicator.

Table 3-1. Field and Laboratory Methods: Benthic Invertebrates Indicator

Variable or Measurement	QA Class	Expected Range and/or Units	Summary of Method	References
Sample Collection	C	NA	One-man kick net used to collect organisms which are composited into riffle and pool samples	RBP (Plafkin et al, 1989) with modification of one-man procedure rather than 2 men
Sorting and Enumeration	C	0 to 500 organisms	Random systematic selection of 300 organisms from sample	
Identification	C	genus or species	Specified keys and references	

C = critical, N = non-critical quality assurance classification.

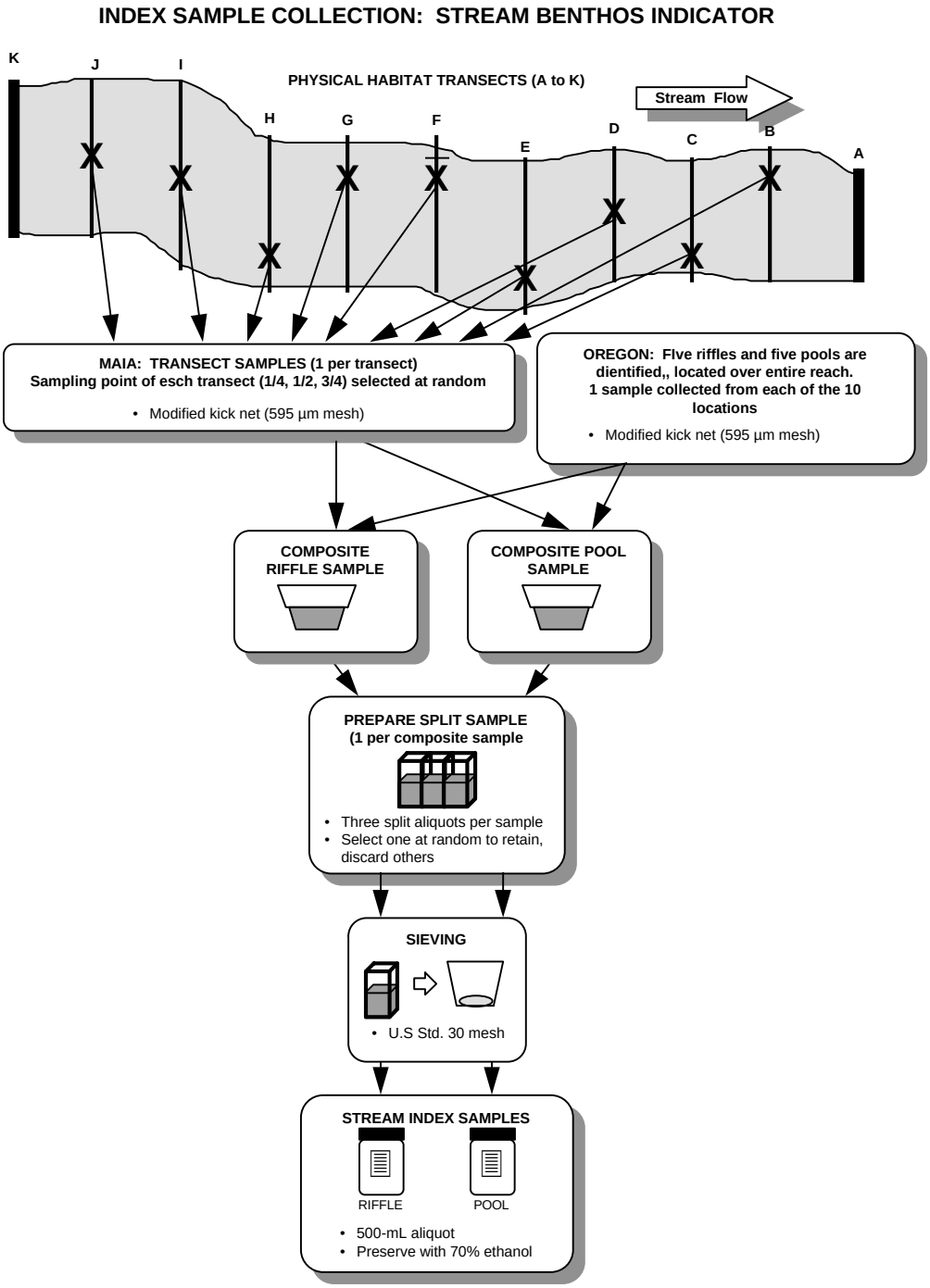

Figure 2-1. Index sampling design for the benthic invertebrates (streams) indicator.

4.0 QUALITY ASSURANCE OBJECTIVES

Measurement data quality objectives (measurement DQOs or MQOs) are given in Table 4-1. General requirements for comparability and representativeness addressed in Part I, Section 2. The MQOs given in Table 4-1 represent the maximum allowable criteria for statistical control purposes. Precision is calculated as percent efficiency, estimated from examination of randomly selected sample residuals by a second analyst and independent identifications of organisms in randomly selected samples. The MQO for picking accuracy is estimated from examinations (repicks) of randomly selected residues by experienced taxonomists.

The completeness objectives are established for each measurement *per site type* (e.g., probability sites, revisit sites,etc.). Failure to achieve the minimum requirements for a particular site type results in regional population estimates having wider confidence intervals. Failure to achieve requirements for repeat and annual revisit samples reduces the precision of estimates of index period and annual variance components, and may impact the representativeness of these estimates because of possible bias in the set of measurements obtained.

Table 4-1. Measurement Data Quality Objectives: Benthic Invertebrates Indicator

Variable or Measurement	Precision	Accuracy	Completeness
Sort and Pick	95%	90%	99%
Identification	95%	90%[a]	99%

NA = not applicable
[a] Taxonomic accuracy, as calculated using Equation 8 in Part I, Section 2.

5.0 QUALITY CONTROL PROCEDURES: FIELD OPERATIONS

Specific quality control measures are listed in Table 5-1 for field operations.

Table 5-1. Field Quality Control: Benthic Invertebrates Indicator

Check or Sample Description	Frequency	Acceptance Criteria	Corrective Action
PRE-SAMPLING			
Inspect kick net	Prior to each use	No holes or tears, no foreign matter on nets	Repair, clean, or replace net as necessary
SAMPLING AND PROCESSING			
Time collection with stopwatch	20 seconds kicking or 60 seconds handpicking	Required time ± 3 seconds to ensure consistency of collection at each site	Add time or repeat sample
Check net	Each collection site	No clinging organisms	Remove any clinging organisms and add to sample

6.0 QUALITY CONTROL PROCEDURES: LABORATORY OPERATIONS

Specific quality control measures are listed in Table 6-1 for laboratory operations. Figure 6-1 presents the general process for collecting and analyzing benthic invertebrate samples.

Table 6-1. Laboratory Quality Control: Benthic Invertebrates Indicator

Check or Sample Description	Frequency	Acceptance Criteria	Corrective Action
SAMPLE PROCESSING (PICK AND SORT)			
Sample residuals examined by different analyst	10% of all samples completed per analyst	Efficiency of picking >95%	If efficiency 90-95%, examine all residuals future samples picked by that analyst until 95% efficiency gained. If <90%, examine all residuals of samples by that analyst and retrain analyst
Split samples sorted and identified by recognized experts	5 to 10% of all samples	Accuracy of contractor laboratory picking and identification >90%	If picking or taxonomic accuracy <90%, all samples in batch will be reanalyzed by contractor
Sample residuals examined by Indicator Lead	Five to ten percent of all samples	If < 300 organisms originally found, examine residuals for additional organisms. If >300 originally found, pick 300 (if possible) from sample and ID to test representativeness of original sample	NA
IDENTIFICATION			
Duplicate identification by different analyst	10% of all samples completed per taxonomist	Efficiency > 95%	If efficiency 90 - 95%, retrain taxonomist. If less than 90, reidentify all samples completed by that taxonomist
Independent identification	All uncertain taxa	Uncertain identifications to be confirmed by expert in particular taxa	Record both tentative and independent IDs
Use standard references	For all identifications	All keys and references used must be on bibliography prepared by Indicator Lead	If other references desired, obtain permission to use from Indicator Lead
Prepare reference collection	All taxa in first batch, all new taxa encountered thereafter	Complete reference collection to be maintained by Indicator Lead	Indicator Lead periodically reviews data and reference collection to ensure reference collection is complete and identifications are accurate

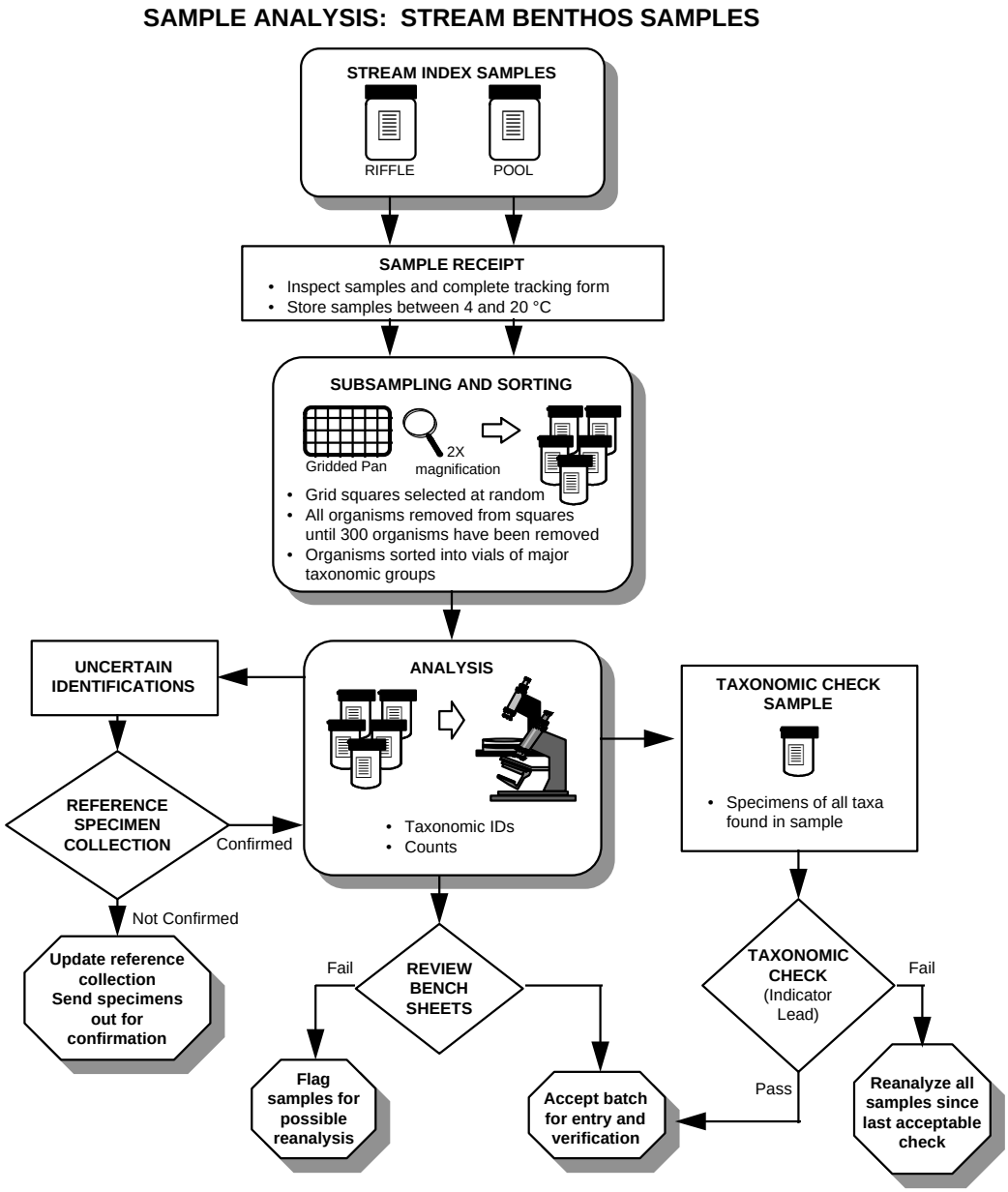

Figure 6-2. Analysis activities for the benthic invertebrates indicator.

7.0 DATA MANAGEMENT, REVIEW, AND VALIDATION

Checks made of the data in the process of review, verification, and validation are summarized in Table 7-1. The Indicator Lead is ultimately responsible for ensuring the validity of the data, although performance of the specific checks may be delegated to other staff members. Once data have passed all acceptance requirements, computerized data files are prepared in a format specified by the EMAP-SW IM Coordinator and copied onto a floppy diskette. The diskettes are transferred to the EMAP-SW IM Coordinator for entry into the centralized data base. A hard copy output of all files accompanies each diskette.

A reference specimen collection is prepared as new taxa are encountered in samples. This collection consists of preserved specimens in vials and mounted on slides and is provided to the responsible EPA laboratory Indicator Lead as part of the analytical laboratory contract requirements. The reference collection is archived at the responsible EPA laboratory.

Sample residuals, vials, and slides are archived by the Indicator Lead until the EMAP-SW TD has authorized, in writing, the disposition of samples. All raw data (including field data forms and bench data recording sheets) are retained in an organized fashion by the Indicator Lead for seven years or until written authorization for disposition has been received from the EMAP-SW TD.

Table 7-1. Data Validation Quality Control: Benthic Invertebrates Indicator

Check Description	Frequency	Acceptance Criteria	Corrective Action
Taxonomic "reasonableness" checks	All data sheets	Species or genera known to occur in given stream conditions or geographic area	Second or third identification by expert in that taxa

8.0 REFERENCES

Klemm, D.J., P.A. Lewis, F. Fulk, and J.M. Lazorchak. 1990. *Macroinvertebrate Field and Laboratory Methods for Evaluating the Biological Integrity of Surface Waters.* EPA 600/4-90/030. U.S. Environmental Protection Agency, Cincinnati, Ohio.

Plafkin, J.L., M.T. Barbour, K.D. Porter, S.K. Gross, and R.M. Hughes. 1989. *Rapid Bioassessment Protocols for Use in Streams and Rivers: Benthic Macroinvertebrates and Fish.* EPA 440/4-89/001. U.S. Environmental Protection Agency, Office of Water, Washington, D.C.

FISH ASSEMBLAGE INDICATOR (STREAMS)

1.0 INTRODUCTION

In addition to the direct relevance of certain species of fish to the assessment endpoint of fishability, the fish assemblage represents a critical component of biological integrity from both an ecosystem function and a public interest perspective. Historically, fish assemblages have been used for biological monitoring in streams more often than in lakes (e.g., Plafkin et al., 1989; Karr, 1991). Fish assemblages can serve as good indicators of ecological conditions because fish are long-lived and mobile, forage at different trophic levels, integrate effects of lower trophic levels, and are reasonably easy to identify in the field (Plafkin et al., 1989). Information collected for EMAP that is related to fish assemblages in streams includes assemblage attributes (e.g., species composition and relative abundance) and incidence of external pathological conditions.

Specific research questions or hypotheses to be addressed from this year's activities, and the data analysis approach to be used are listed in Table 1-1.

2.0 SAMPLING DESIGN

The index sampling designs for streams is illustrated in Figure 2-1. The objective for index sampling is to obtain a sample of the extant fish assemblage that includes all common and less abundant species in relative proportions to their actual abundance in the stream. For streams, a series of samples is collected from all available habitat types present in a designated stream reach (40 times the mean width) during a specified level or duration of sampling effort (electrofishing and seining). The entire series of samples considered collectively comprises the index sample for the lake or stream.

3.0 SAMPLING AND ANALYTICAL METHODOLOGIES

Sample Collection: In streams, the primary methods of fish collection are by electrofishing and seining. Generally the entire stream reach is fished or a set amount of time is spent fishing. Collection methods are based on standard procedures recommended by professional organizations such as the American Fisheries Society (Nielsen and Johnson, 1983) and those published by EPA (Klemm et al., 1993) for use in evaluating biological integrity of aquatic systems (primarily lotic). All of the fish catch is tallied, although only selected specimens are retained. These include voucher specimens and unknown or uncertain taxa and hybrids. Detailed procedures for fish collection and preparing voucher specimens are contained in the streams and lakes field operations manual.

Table 1-1. Research Questions and Hypotheses for Streams: Fish Assemblage Indicator

Question or Hypotheses	Data Analysis Approach:
EMAP Design Evaluation: Obtain estimates for annual and index period variations	Repeat sampling of streams during index period, and revisits to streams sampled in previous year(s)..
Indicator Development and Evaluation: Continue evaluation of sampling methods effectiveness in obtaining representative samples. Develop index sampling design and methods for collecting samples from non-wadable streams and rivers	Development of return/effort curves for various gear types and reach lengths Comparison of EMAP surface water sampling results with available historical data.
Suitability of multivariate indicator(s) of condition.	Relationships between fish assemblage attributes and environmental conditions will be developed and explored using multivariate multivariate ordination techniques (e.g., detrended correspondence analysis and canonical correspondence analysis), including spatial autocorrelation analysis and Mantel test for comparisons of similarity and diversity matrices.
Suitability of multimetric indicator(s) of stream condition	Metrics based on different attributes of assemblage structure and function will be evaluated for inclusion into an overall index of biotic integrity for stream condition following the approach developed by Karr et al. (1986). Candidate metrics include species richness, number of exotic species present, percent of species belonging to various trophic guilds, percent of species belonging to various tolerance guilds, percent of species belonging to various habitat guilds, or percent of species with various types of life history and reproductive strategies.

Field Measurements: Field measurements, summarized in Table 3-1, include fish tallies, measurement of selected physical characteristics (length, weight), field identification, and recording of observations of external abnormal characteristics related to pathological conditions. As with sample collection, all field measurements are based on standard procedures recommended by professional organizations and those published by EPA. Detailed procedures for field measurements and completion of standardized recording forms are described in the field operations manuals.

Analysis: There are no analytical methods associated with the fish assemblage indicator. Voucher specimens and specimens of uncertain taxa are verified by independent taxonomic expert. Voucher specimens are maintained as part of permanent museum collections.

INDEX SAMPLE COLLECTION (STREAMS): FISH ASSEMBLAGE INDICATOR

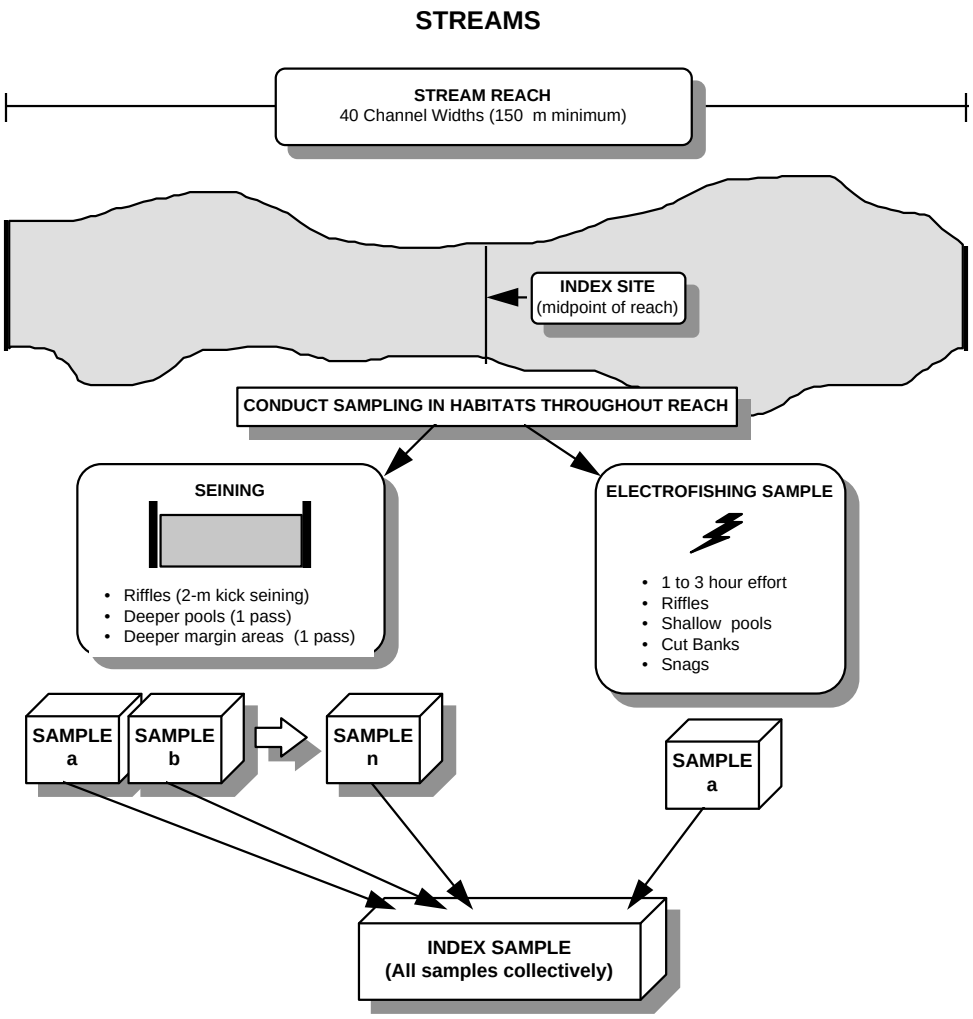

Figure 2-1. Stream index sampling design for the fish assemblage indicator.

Table 3-1. Field Measurement Methods: Fish Assemblage Indicator

Variable or Measurement	QA Class	Expected Range and/or Units	Summary of Method	References
Species Composition	C	Species per sample or unit effort	Collection within defined length of stream channel (or adjustment for time spent sampling) by active sampling gear (electrofishing and seining). Taxonomic identification and enumeration in field or at museum facility.	Nielsen and Johnson (1983); Klemm et al. (1993); Cowx and Lamarque (1990)
Relative Density	C	catch per unit effort (CPUE)[a]	Number of individuals collected as a function of sampling time or amonunt of stream sampled.	
Total length Standard Length	N	mm	Direct measurement of subsample (20 individuals) per species. For lakes, only species with adult lengths exceeding 100 mm are considered for measurement.	Nielsen and Johnson (1983); Klemm et al. (1993)
Frequency of external anomalies	N	No. occurrences per sample	Visual examination during identification.	Nielsen and Johnson (1983); Klemm et al. (1993)

C=Critical, N=Non-critical QA measurement classification.
[a] Catch per unit effort for stream sampling can be defined based on: (1) duration of sampling effort for samples collected by electrofishing and area sampled for samples collected by seining, or (2) length or area of stream sampled.

4.0 QUALITY ASSURANCE OBJECTIVES

Measurement data quality objectives (measurement DQOs or MQOs) are given in Table 4-1. General requirements for comparability and representativeness addressed in Part I, Section 4. The MQOs given in Table 4-1 represent the maximum allowable criteria for statistical control purposes. Precision objectives are established only for fish length measurements; it is estimated as the coefficient of variation from repeated length determinations on individual fish. Taxonomic accuracy is estimated based on independent identifications of voucher specimens by experienced ichthyologists using equations presented in Part I, Section 2 (Equations 8, 9 , or 10). As additional qualified personnel become available, accuracy checks will be performed in the field concurrently with determinations made by field crews. No objective for accuracy of external anomaly determinations is currently defined, although accuracy can be estimated, if desired, by concurrent measurements of samples by field personnel or experienced ichthyologists using the equations for taxonomic accuracy, but substituting the specific types of anomalies identified in place of species.

Table 4-1. Measurement Data Quality Objectives: Fish Assemblage Indicator

Variable or Measurement	Precision	Accuracy	Completeness
Species Composition and Relative Density	NA	±90%	90%
Length Measurements	±10%	NA	90%
Frequency of external anomalies	NA	NA	90%

NA = not applicable

The completeness objectives are established for each measurement *per site type* (e.g., probability sites, revisit sites, etc.). Failure to achieve the minimum requirements for a particular site type results in regional population estimates having wider confidence intervals. Failure to achieve requirements for repeat and annual revisit samples reduces the precision of estimates of index period and annual variance components, and may impact the representativeness of these estimates because of possible bias in the set of measurements obtained.

5.0 QUALITY CONTROL PROCEDURES: FIELD OPERATIONS

5.1 Voucher Specimens

General quality control activities and requirements pertaining to the collection of fish assemblage samples from streams are presented in Table 5-1. Standard levels of sampling effort are established for electrofishing and seining activities based on the length of stream reach and available habitats (Table 5-2). Figure 5-1 presents the general process for collecting and analyzing fish assemblage samples from streams. Collection and handling procedures for fish assemblage samples to ensure compliance with these requirements are documented in the stream field operations manuals. Guidelines and requirements associated with sample labeling and tracking are presented in Section 7.0 and in Part I, Section 6.

Table 5-3 presents quality control activities associated with field analysis of fish assemblage samples collected from streams. Specimens that cannot be confidently identified by a field crew are preserved as a separate sample as part of the voucher collection for the stream. Specimens with external pathological characteristics that are uncertain to the observer are examined by a second crew member for discussion and confirmation. No duplicate examinations of specimens are required.

Table 5-1. Quality Control Activities for Stream Sampling: Fish Assemblage Indicator

QC Activities	Requirements
Use and maintenance of sampling gear	All personnel are trained in the use and maintenance of all types of sampling gear. Personnel who will be collecting fishes by electrofishing should participate in an electrofishing training course offered by the U.S. Fish and Wildlife Service, or a course of comparable content offered by another qualified organization. Sampling operations are conducted in accordance with all mandated safety requirements. Inspect all electrofishing equipment before each use for proper and safe operation.
Collecting Permits	Field crews conduct sampling operations in accordance with all federal and state legal requirements associated with the collection of fish for scientific purposes. The sampling crew carries appropriate state and federal collection permits at all times and observes any restrictions regarding the use of specific types of sampling gear.
Sampling locations	Sampling activities begin at downstream end of reach and progresses upstream. All available and accessible habitat types are sampled.
Electrofishing	Set voltage based on conductivity of water. Use minnow seines as block nets when necessary to prevent loss of specimens.
Seining	Mesh size= 0.6 cm Pull seine downstream in pools.

Table 5-2. Required Levels of Sampling Effort for Streams: Fish Assemblage Indicator

Type of Sampling	Length/Area Sampled	Duration of Sampling
Electrofishing	40 channel widths as measured at index site. Minimum length=150 m Maximum length=500 m	Minimum= 1 hour Maximum= 3 hours
Seining	Kick seining (riffles): begin 2 m upstream from net Pool seining in deeper pools	

SAMPLE ANALYSIS: STREAM FISH ASSEMBLAGE SAMPLES

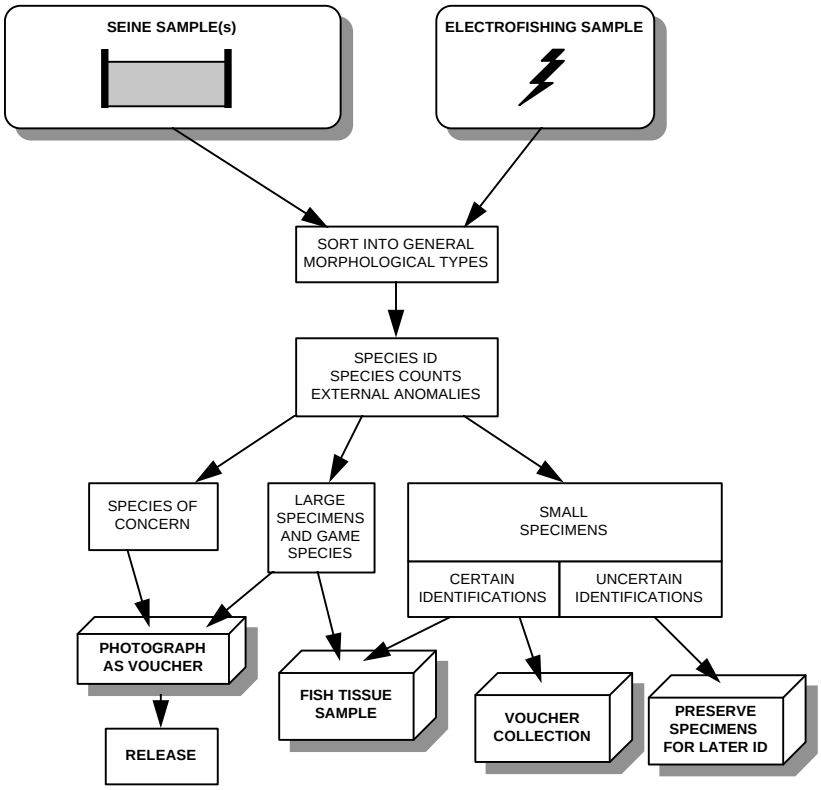

Figure 5-2. Stream sample collection and field analysis activities for the fish assemblage indicator.

Table 5-3. Quality Control Activities for Analyses of Stream Samples: Fish Assemblage Indicator

Quality Control Activity	Description and Requirements	Corrective Action
Taxonomic Proficiency	Trained by an experienced ichthyologist to identify common fishes in the region. All personnel are evaluated for proficiency by an experienced ichthyologist prior to any sample collection.	Provide additional training as necessary.
Taxonomic references and keys	Appropriate state or regional fish taxonomic references should be available for use by all field crews.	
Taxonomic IDs	Specimens of uncertain identification are reviewed by second crew member with appropriate taxonomic expertise.	Specimens that cannot be confidently identified are preserved as "unknown" for later identification at a laboratory or museum.
Species counts	Count data are reviewed by a second crew member to ensure all individuals collected are accounted for on data sheets.	Correct errors on data collection form.
External anomalies:	Anomalies identified are reviewed by a second crew member.	Uncertain determinations are qualified and specimen(s) preserved as part of voucher collection.

Table 5-4. Quality Control Activities for Preparing Voucher Specimens from Stream Fish Samples.

Quality Control Activity	Guidelines and Requirements
Species vouchered	All small species (excepted endangered), small individuals of larger species, hybrids, and uncertain identifications
Number and size of voucher specimens	Voucher up to 25 individuals of each species; if less than 25 individuals are taken, retain all specimens. Keep 1 or 2 small individuals or larger species. Voucher live specimens whenever possible.
Use of photographs as voucher specimens	Photograph all specimens on measuring board so length can be determined from picture. Larger specimens of common game and sport fish are photographed and released. Species of concern should be photographed and released
Sample containers	4-L Nalgene jars used (generally two per stream; one is for unknown taxa) Specimens of each species placed in perforated heavy zip-locking plastic bags Containers should not be overfilled with specimens to permit adequate fixation and preservation. Larger specimens should not be forced into container so they become fixed in a curved position.

(continued)

Table 5-4. (Continued)

Quality Control Activity	Guidelines and Requirements
Preservation	10% formalin buffered with borax (pH 7 to 8) Large specimens (>100 mm) slit along right side.
Transport and Shipping	Keep all bottles from single stream together when transporting or shipping. Ship or transport in UN-approved containers that maintain required storage conditions. NOTE: Transport or shipment of formalin-preserved samples may be considered hazardous materials, requiring special labelling and manifesting.

6.0 QUALITY CONTROL PROCEDURES: LABORATORY AND MUSEUM OPERATIONS

For the fish assemblage indicator, laboratory operations refer to activities conducted at museums or other similar facilities responsible for confirming taxonomic identifications of specimens submitted by field crews and for permanent archival of voucher specimens. Table 6-1 provides general requirements for receiving, processing, and analyzing of fish voucher specimen samples.

7.0 DATA MANAGEMENT, REVIEW, AND VALIDATION

Checks made of the data in the process of review, verification, and validation are summarized in Table 7-1. The Indicator Lead is ultimately responsible for ensuring the validity of the data, although performance of the specific checks may be delegated to other staff members. As additional resources become available for more thorough verification and validations, additional activities will be implemented. Examples of such activities include producing summary statistics of sampling data, exploratory data analyses (e.g., box and whisker plots) of species richness and relative abundance data. Internal consistency checks for commonly co-occurring taxa (e.g., warmwater vs. coldwater species)and for the absence of expected guild or trophic group species will be implemented once sufficient data are available to develop predictive relationships.

Table 6-1. Laboratory and Museum Quality Control: Fish Assemblage Indicator

Quality Control Activity	Description and Requirements	Corrective Action
Sample Storage	Store samples in well ventilated area at 4 to 20 °C. Monitor temperature weekly.	Qualify sample as suspect for all analyses
Holding time	Complete processing bulk samples within 48 hours of collection	Qualify samples
Preservation	Transfer specimens from 10% formalin to 70% ethanol after leaching for several days in water.	
Holding Times for ethanol-preserved samples	Indefinite, depending on original preservation, holding conditions, and curation practices.	
Sample processing	Process one sample at a time. Maintain sample integrity during processing (i.e., keep specimens from single field sample together until all identifications for a given lake or stream are completed.)	
Taxonomic IDs	Specimens of uncertain identification are reviewed by senior taxonomist. Specimens that cannot be confidently identified are sent to independent taxonomic expert for confirmation.	

Table 7-1. Data Validation Quality Control: Fish Assemblage Indicator

Activity or Procedure	Requirements and Corrective Action
For individual variables: Range checks of count data. Frequency checks of taxonomic codes used for data entry and external anomaly codes. Correct spellings of common and scientific names. Review any field or museum qualifiers assigned to identification or count value	Correct reporting errors or qualify as suspect or invalid.
Sum of individuals measured, vouchered, and counted sums to total collected Adequate sampling effort, (number and types of gear) including seining and judgement sampling	Qualify data as suspect or invalid.
Review data from taxonomic confirmations from museums.	Correct identification errors and associated counts, or qualify data as suspect or invalid.
Summarize and review species collected and relative abundances across all samples.	Compare with results from other years to determine comparability. Determine impact and possible limitations on overall usability of data

8.0 REFERENCES

Cowx, I.G., and P. Lamarque (eds.). 1990. *Fishing with Electricity: Applications in Freshwater Fisheries Management.* Fishing News Books, Oxford, England, 248 pp.

Karr, J.R., K.D. Fausch, P.L. Angermeier, P.R. Yant, and I.J. Schlosser. 1986 Assessing biological integrity in running waters: a method and its rationale. *Illinois Natural History Survey Special Publication No. 5.* Illnois Natural History Survey, Champaign, Illinois, 29 pp.

Karr, J.R. 1991. Biological integrity: a long neglected aspect of water resource management. *Ecological Applications* 1(1):66-84.

Klemm, D.J., Q.J. Stober, and J.M. Lazorchak. 1993. *Fish Field and Laboratory Methods for Evaluating the Biiological Integrity of Surface Waters.* EPA 600/R-92/111. U.S. Environmental PRotection Agency, Cincinnati, Ohio.

Neilsen, L.A., and D.L. Johnson (eds.). 1983. *Fisheries Techniques.* American FIsheries Society, Bethesda, Maryland, 468 pp.

Plafkin, J.L., M.T. Barbour, K.D. Porter, S.K. Gross, and R.M. Hughes. 1989. *Rapid Bioassessment Protocols for Use in Streams and Rivers: Benthic Macroinvertebrates and Fish.* EPA 440/4-89/001. U.S. Environmental Protection Agency, Washington, D.C.

FISH TISSUE CONTAMINANT INDICATOR

1.0 INTRODUCTION

Contaminants in fish tissue acquired through direct uptake or indirectly through food chains potentially affect both the fishability and biotic integrity of lakes and streams. The long-term objectives for this indicator are to develop wildlife and human exposure hazard estimates, by comparing estimated exposure (*E*; from U.S. EPA, 1989a) from measured concentrations of contaminants in target fish species samples combined with information regarding potential consumers, to available information on safe consumption levels:

$$E \quad \frac{(C_t \cdot I \cdot X_m)}{W}$$

where C_t is the measured concentration of contaminant in tissue (in mg/kg fresh weight), I is the estimated mean daily consumption rate (in kg/day), X_m is a relative absorption coefficient (dimensionless), and W is the average weight of a consumer.

Specific research questions and hypotheses to be addressed from this year's activities are listed in Table 1-1.

Table 1-1. Research Questions and Hypotheses: Fish Tissue Contaminants Indicator

EMAP Design Evaluation: Determine the most appropriate approach to formulate regional-scalestream population estimates based on risk from fish tissue contamination Obtain estimates of iportant variance components from repeat visit sampling
Indicator Development and Evaluation: Evaluate the representativeness of compositing individuals within a target species into a single index sample, the reproducibility of the sampling process, and the relative bioaccumulation rates in small and large fish species
Other Evaluation: Obtain estimates of variability associated with sample collection and laboratory analysis of tissue contaminants

2.0 SAMPLING DESIGN

At each stream, composite index samples of selected target species are prepared from individuals collected from throughout the stream reach, if possible. When available, two composite samples are collected from stream reaches; one comprised of small fish and the other comprised of individuals of a larger, long-lived species.

3.0 SAMPLING AND ANALYTICAL METHODOLOGIES

Sample Collection: Selected target species are retained from the fish assemblage indicator sampling. Detailed procedures for fish collection, lists of target species, and minimum and desired sample sizes are presented in the field operations manuals. A fish tssue sample usually consists of 3 to 5 large individuals or 20 to 200 small fish, which are composited in the laboratory. With occasional exceptions, samples consist of fish of the same species and approximately the same size. Samples are stored on dry ice or ice until shipment to the analytical laboratory.

Analysis: At the analytical laboratory, the fish are composited, processed, and analyzed by the methods summarized in Table 3-1 for metals, Table 3-2 for pesticides, and Table 3-3 for PCB congeners. For the Oregon stream survey, only mercury analyses are currently planned. Any of the listed reference methods may be used, provided results are obtained which meet or exceed the detection limit and performance objectives listed in section 4. Additional information on analytical methods is provided in the laboratory methods manuals. Maximum holding times for frozen whole fish have not been established; all EMAP fish tissue samples should be analyzed within one year of date of collection, if possible.

Table 3-1. Analytical Methods for Metals: Fish Tissue Contaminants Indicator

Analyte (CAS No.)[a]	Detection Limit (ng/g)[b]	Summary of Method	References
Aluminum (7429-90-5)	10	Digestion with hot HNO_3 and H_2O_2. Analysis by graphite furnace atomic emission spectrometry (GFAAS) or inductively coupled plasma (ICP)	EPA 200.3 (rev. 1); EPA 200.11 (EPA, 1991a); McDaniel, 1990; EPA, 1989b; CLP (EPA, 1991b); APHA, 1989; EPA 7000 series (EPA, 1990a)
Arsenic (7440-38-2)	2.0		
Cadmium (7440-43-9)	0.2		
Chromium (7440-47-3)	0.1		
Copper (7440-50-8)	5.0		
Iron (7439-89-6)	50.0		
Lead (7439-92-1)	0.1		
Nickel (7440-02-0)	0.5		
Selenium (7782-49-2)	0.1		
Silver (7440-22-4)	0.01		
Tin (7440-31-5)	0.05		
Zinc (7440-66-6)	50.0		
Mercury (7439-97-6)	0.01	Digestion with hot HNO_3 and H_2O_2. Analysis by cold vapor atomic absorption spectrometry	EPA 200.3 (rev. 1), EPA 245.6 (rev. 1)

[a] Chemical Abstract Services (CAS) registration number.
[b] Units are ng/g fresh tissue weight.

Table 3-2. Analytical Methods for Pesticides: Fish Tissue Contaminants Indicator

Analyte (CAS No.)[a]	Detection Limit (ng/g)[b]	Summary of Method	References
Aldrin (309-00-2) Chlordane-*cis* (5103-71-9) Chlordane-*trans* (5103-74-2) 2,4'-DDD (53-19-0) 4,4'-DDD (72-54-8) 2,4'-DDE (3424-82-6) 4,4'-DDE (72-55-9) 2,4'-DDT (789-02-6) 4,4'-DDT (50-29-3) Dieldrin (60-57-1) Endosulfan-I (959-98-8) Endosulfan-II (33213-65-9) Endrin (72-20-8) Heptachlor (76-44-8) Heptachlor Epoxide (1024-57-3) Hexachlorobenzene (118-74-1) Hexachlorocyclohexane [Gamma-BHC/Lindane] (58-89-9) Mirex (2385-85-5) *trans*-Nonachlor (3765-80-5) *cis*-Nonachlor (5103-73-1) Oxychlordane (27304-13-8)	1	Soxhlet extraction into hexane/methylene chloride; analysis by gas chromatography/electron capture detection (GC/ECD) recommended	EPA 608 (NOAA, 1988); EPA 682 (NOAA, 1988); CLP (EPA, 1991c)

[a] Chemical Abstract Services (CAS) registration number.

[b] Units are ng/g fresh tissue weight.

Table 3-3. Analytical Methods for PCB Congeners: Fish Tissue Contaminants Indicator

Analyte (CAS No.)[a]	Detection Limit (ng/g)[b]	Summary of Method	References
2,4-Dichlorobiphenyl #8 (34883-43-7) 2,2',5-Trichlorobiphenyl #18 (37680-65-2) 2,4,4'-Trichlorobiphenyl #28 (7012-37-5) 2,2',5,5'-Tetrachlorobiphenyl #52 (35693-99-3) 2,2',3,5'-Tetrachlorobiphenyl #44 (41464-39-5) 2,3',4,4'-Tetrachlorobiphenyl #66(32598-10-0) 2,2',4,5,5'-Pentachlorobiphenyl #101 (37680-73-2) 2,3',4,4',5-Pentachlorobiphenyl #118 (31508-00-6) 2,3,3',4,4'-Pentachlorobiphenyl #105 (32598-14-4) 2,2',4,4',5,5'-Hexachlorobiphenyl #153 (35065-27-1) 2,2',3,4,4',5-Hexachlorobiphenyl #138 (35065-28-2) 2,2',3,4',5,5',6-Heptachlorobiphenyl #187 (52663-68-0) 2,2',3,3',4,4'-Hexachlorobiphenyl #128 (38380-07-3) 2,2',3,4,4',5,5'-Heptachlorobiphenyl #180 (35065-29-3) 2,2',3,3',4,4',5-Heptachlorobiphenyl #170 (35065-30-6) 2,2',3,3',4,4',5,6-Octachlorobiphenyl #195 (52663-78-2) 2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl #206 (40186-7-2-9) Decachlorobiphenyl #209 (2051-24-3) 3,3',4,4'-Tetrachlorobiphenyl #77[c] (32598-13-3) 3,3',4,4',5-Pentachlorobiphenyl #126[c] (??) 3,3',4,4',5,5' Hexachlorobiphenyl #169[c] (32774-16-6)	1	Soxhlet extraction into hexane/ methylene chloride; analysis by gas chroma-tography/electron capture detection (GC/ECD) recommended	EPA 682 (NOAA, 1988); 8080A (EPA, 1990b)

[a] Chemical Abstract Services (CAS) registration number.
[b] Units are ng/g fresh tissue weight.
[c] Coplanar PCBs.

4.0 QUALITY ASSURANCE OBJECTIVES

Measurement data quality objectives (measurement DQOs or MQOs) are given in Table 4-1. General requirements for comparability and representativeness addressed in Part I, Section 4. The MQOs given in Table 4-1 represent the maximum allowable criteria for statistical control purposes. Precision is estimated from the standard deviation (or relative standard deviation, Equation 4-4) of repeated measurements of QC samples, such as calibration check samples, internal reference standards, and standard reference materials, or from replicate sample measurements. Bias is determined as described in Section 4 (Equations 4-8 and 4-9) using a set of replicated measurements of one or more samples of known composition, such as a standard or certified reference material. Accuracy objectives are based on analyses of Standard Reference Materials (SRMs) and spiked (fortified) samples, and on recovery of surrogate organic compounds. Accuracy is calculated using Equation 4-10. For inorganic analyses, accuracy objectives are established as 100 ± 15 percent. For organic compounds, accuracy objectives are established as 100 ± 50 percent for both fortified samples and for surrogate compounds.

The completeness objectives are established for each measurement *per site type* (e.g., EMAP sites, Revisit sites, REMAP sites). Failure to achieve the minimum requirements for a particular site type results in regional population estimates having wider confidence intervals. Failure to achieve requirements for repeat and annual revisit samples reduces the precision of estimates of index period and annual variance components, and may impact the representativeness of these estimates because of possible bias in the set of measurements obtained.

Required method detection limits (MDLs) for each of the analytes were presented in Tables 3-1, 3-2, and 3-3. Detection limits are calculated using equiation 1 in Part 1, Section 2 For metals, MDLs for each analyte are determined by replicate determinations of a low-level standard that is carried through the entire sample preparation and analysis procedure. The concentration of analyte in the standard should be between two and three times the MDL values in Table 3-1. Samples are processed through the entire analytical procedure. For inorganic analyses, background levels measured in laboratory reagent blank samples must be less than the MDL value presented in Table 3-1. For organic analyses, background values of compounds measured in reagent blank samples cannot exceed three times the MDL values presented in Tables 3-2 and 3-3.

Table 4-1. Measurement Data Quality Objectives: Fish Tissue Contaminants Indicator

Variable or Measurement	Precision	Accuracy or Bias	Completeness
Metals Analysis	MDL or ±15% percent, whichever is larger	MDL or ±15% percent, whichever is larger	90%
Organic Analyses	MDL or ±30% percent, whichever is larger	MDL or ±30% percent, whichever is larger	90%

5.0 QUALITY CONTROL PROCEDURES

Specific quality control measures are listed in Table 5-1 for field operations.

Table 5-1. Field Quality Control: Fish Tissue Contaminants Indicator

Check or Sample Description	Frequency	Acceptance Criteria	Corrective Action
SAMPLING AND PROCESSING			
Measure fish length	Each fish (except small fish)	Length of the smallest fish should be at least 75 percent of length of the largest specimen	Include smaller fish and flag sample; prepare second sample of next available priority species
Check temperature of storage/ shipping container	Once per day	Temperature should be 4 EC or below	Add or remove dry ice/ice

6.0 QUALITY CONTROL PROCEDURES: LABORATORY OPERATIONS

Quality assurance and quality control procedures and measurements associated with analyses of fish tissue samples are documented in the respective EPA methods and include such items as use of ultrapure reagents, calibration procedures, procedures for dilution and analysis of samples exceeding the calibration range, and preparation and analysis of QC samples. Table 6-1 lists the QC procedures specific to EMAP surface waters research and Table 6-2 lists QA/QC samples used in EMAP surface water analyses.

All occurrences of laboratory statistical control loss based on check sample measurements are noted in the instrument logbook and reported to the on-site QA coordinator. Corrective action is taken and statistical control is reestablished before further routine sample analyses are performed. Data not associated with demonstrated statistical control are unacceptable without an explanation of why control was not reestablished. Original data associated with unacceptable QCCS measurements are recorded in the logbook, although only values associated with acceptable QCCS measurements are eventually entered into the computerized data base.

7.0 DATA MANAGEMENT, REVIEW, AND VALIDATION

Checks made of the data in the process of review, verification, and validation are summarized in Table 7-1. The Indicator Lead is ultimately responsible for ensuring the validity of the data. Specific checks of analytical data are completed by analytical laboratory personnel. A data submission package is delivered to the Indicator Lead within a specified timeframe following sample receipt (generally 45 days). The data submission package includes the following:

Table 6-1. Laboratory Quality Control: Fish Tissue Contaminants Indicator

Quality Control Activity	Description and Requirements	Corrective Action
SAMPLE RECEIPT AND STORAGE		
Check temperature of storage area	Check temperature daily or by automated alarm system; should be -20 ± 2EC	Adjust as necessary
SAMPLE PROCESSING		
Use clean workstation	Workstation suitable for trace element work	Any samples not prepared in workstation must be flagged as possibly contaminated
Utensils	All utensils should be composed of quartz, TFE, or ceramic (polypropylene or polyethylene may be used for inorganic); dissection tools of high-quality corrosion-resistant stainless steel or titanium; glass or TFE cutting boards and containers	Tools of these materials must be used and cleaned properly to avoid contamination
Clean glassware, scalpels, and other tools	All glassware and tools must be contaminant-free; clean with reagent-grade distilled water, acid soak (inorganic), and solvent (organic)	Flag any samples not prepared with clean glassware and tools
Rinse fish	Rinse each fish in reagent-grade distilled water	This step is necessary to remove any external contamination from field and shipping

- A letter by the laboratory manager or on-site QA coordinator, indicating the samples were analyzed according to approved methodologies and in accordance with requirements stated in the QAPP. All deviations from approved protocols or methods require the authorization of the Indicator Lead, contract Project Officer (if applicable), and EMAP surface waters QA staff prior to sample analysis.

- Analytical data, reported according to the criteria, medium, and structure approved by the EMAP surface waters information management staff. For metals analyses, results are reported as ng/g fresh tissue

Table 6-2. Quality Control Samples: Fish Tissue Contaminants Indicator

Sample Description	Frequency	Acceptance Criteria	Corrective Action
PRE-AWARD PROFICIENCY TESTING			
Analysis of PE samples or SRMs	Prior to sample analysis	Results must be within precision, bias, and accuracy DQOs. For organic analyses, retention times of target compounds must also be confirmed	Repeat proficiency test or eliminate laboratory from consideration
ANALYSES			
Reagent Blank	Each batch, prior to sample analysis	Measured analytes < 3X the MDL or < ±30% of sample levels	Find and remove source of contamination
QCCS	Each batch, prior to sample analysis, every 10th sample or shorter interval, after last sample analysis	Results < ±25% for a single analyte, or < ±15% on average for all analytes	Repeat QCCS. If out-of-control still indicated, recalibrate, repeat analyses since last successful QCCS
Internal Reference Sample-NIST SRM 1974 (or equivalent)	One per extraction batch	< ±15% of SRM reference value (inorganic); < ±30% (organic)	Reprocess all samples in batch
Matrix Spike Sample	One per extraction batch	< 50% recovery	Reprocess all samples in batch
Matrix Spike or Laboratory replicate	One per extraction batch	Relative percent difference < ± 30%	Reprocess all samples in batch
External PE samples	One to three times per year	Comparison between referee and analytical laboratory < 30%	
DDT Breakdown Check	Weekly	< 20 %	Clean injection port and reassess breakdown
Surrogate Compounds (organic analyses only)	Every sample	> 50% recovery	Target compounds adjusted based on surrogate recovery as internal calibration or external manual adjustment

Table 7-1. Data Validation Quality Control: Fish Tissue Contaminants Indicator

Check Description	Frequency	Acceptance Criteria	Corrective Action
DATA ENTRY			
Bench Sheet/Logbook checks	Each sample	All entries legible, accurate, complete	Correct bench sheet or reanalyze sample
Data Entry Checks (duplicate entry or 100% check against original logbook)	All entries	All data correctly entered	Correct entries
DATA VERIFICATION CHECKS			
Automated range checks/frequency distributions	All applicable data	All values within expected range/frequency	Check original logbook entry; reanalyze sample and/or flag data value
Check sample holding times	Each analyte	Analysis completed within critical holding time	Flag data

weight. Results are reported to three significant figures. For organic analyses, results are reported after adjustment based on surrogate sample analyses. Adjusted results are reported as ng/g fresh tissue weight. Results are reported to three significant figures. Results below the MDL should be reported as measured, but qualified to indicate the value is below the MDL. In addition, results from samples that produce an instrument response (i.e., that are greater than zero concentration), but that cannot be quantified by the instrument, should be reported and qualified as detectable but not quantifiable.

- Results of associated QC data, including control charts (if requested), and summary report that identifies any problems that were discovered during laboratory review and what corrective actions were implemented.

Tissue samples remaining after processing into homogenates that have not been extracted are maintained frozen (-20 EC) until all analyses have been completed and the results verified for accuracy. Samples are archived until the EMAP Director has authorized, in writing, the disposition of samples. All raw data (including laboratory notebooks and bench data recording sheets) are retained in an organized fashion for seven years or until written authorization for disposition has been received from the EMAP Director.

8.0 REFERENCES

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